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PROPERTIES OF LIQUID FOOD COMPONENTS IN AQUEOUS SOLUTION AND THEIR BEHAVIOR DURING FREEZE DRYING

by

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A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF FOOD SCIENCE

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FALL, 1977

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

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in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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Date June 20, 1977

To Helga

ABSTRACT

Some physical properties of liquid food components in model aqueous solutions were investigated. Diffusion coefficients of a sugar (sucrose), an amino acid (glycine) and a polyfunctional alcohol (glycol) were measured at 25°C by using the schlieren optical system of a preparative ultracentrifuge. The schlieren optical system was modified by the incorporation of a 35 mm single lens reflex camera. The diffusion coefficients, obtained from a 10 min experiment, were well within 2% of values found in existing literature and had an intrinsic precision of better than 2%. The technique was found to be sensitive enough to monitor the variation of diffusion coefficients with small changes in solute concentration and temperature.

The solubilities of the sparingly soluble essential oil components, piperitone, pulegone and carvone, were determined in aqueous solutions containing dissolved sucrose, glucose or sodium chloride. All dissolved solids were found to reduce the solubility of the essential oil components. Studies conducted at 10, 20 and 30°C showed that the solubilities of piperitone and pulegone increased with a decrease in temperature,

whereas carvone exhibited a solubility minimum close to 20°C. Calculated enthalpies, free energies and entropies were compatible with the current theories of dilute aqueous solutions.

The retentions of terpenic essential oil components (piperitone, pulegone and carvone) and non-terpenic essential oil components (eugenol and m-anisaldehyde) were measured during freeze drying of model aqueous solutions. Model solutions contained sucrose, glucose, sodium chloride and gum arabic which are all common food components. Retention of the essential oil components was found to be dependent on; solids concentration, solids composition, sample thickness, initial volatile content, the presence of additional volatiles, freezing rate and solution pH.

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I. Measurement of Diffusion Coefficients of Low Molecular Weight Compounds in Aqueous Solution Using an Ultracentrifugal Technique

A. INTRODUCTION

For many years quantitative diffusion measurements have greatly added to the knowledge of molecular weight and characteristic properties of proteins and other macromolecules of biological interest. In addition diffusion studies have become increasingly important in other areas; extraction, absorption, distillation and ion exchange (Holmes, 1960). Correlation of mass-transfer coefficients requires a knowledge of diffusion coefficients. For example, the diffusion phenomenon has been successfully applied to various food processing techniques in an attempt to explain the mass-transfer characteristics of food components during processing. The degree of volatile retention in spray drying (Rulkens and Thijssen, 1972b), air drying (Menting et al., 1970b) and freeze drying (Thijssen, 1972b and King and Chandrasekaran, 1973) has been explained in terms of diffusion theories.

Diffusion may be defined as the process whereby concentration differences in a solution spontaneously decrease until the solution finally becomes homogeneous.

Diffusion occurs because molecules in a solution are in constant motion, this continual wandering being a direct consequence of their thermal energy. The term diffusion is applied only to the macroscopic flow of solution components due to concentration differences, whereas the random movements of individual molecules through the solution, which occur after the solution has reached macroscopic homogeneity, are not referred to as diffusion.

Fick's first law, as denoted by Equation (1) for

$$J_1 = -D\left(\frac{\partial c_1}{\partial x}\right) \qquad (1)$$

one dimensional transport of solute, defines the diffusion coefficient, D, in terms of flux of solute, J ($kgm^{-2}s^{-1}$) and its concentration gradient. A straightforward calculation of D is not possible since only concentration gradients may be measured directly whereas flow of solute is not susceptible to direct measurement. Most methods for determining D utilize integrated forms of Fick's second law, Equation (2), or Equation (3) if D varies appreciably with concentration.

$$\frac{\partial ci}{\partial t} = D\,\frac{\partial^2 ci}{\partial xi^2} \qquad (2)$$

$$\frac{\partial ci}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial ci}{\partial xi}\right) \qquad (3)$$

B. LITERATURE REVIEW

This section will deal mainly with techniques used to determine diffusion coefficients in binary liquid systems of non-electrolytes. Diffusion in electrolytic solutions has been reviewed by Harned (1947). Miller (1959) and Gosting (1956) have reviewed diffusion in three component systems. In his review article Gosting (1956) also presents an excellent review of binary diffusion.

Diffusion measurements may be classified into three main types. The first type to be considered include techniques where diffusion occurs in a quasi-stationary state and it is possible to measure the diffusion rate and concentration gradient. The second type includes techniques where a given initial concentration distribution at a starting time is known and the concentration distribution at the end of the experiment is determined. In the third type the concentration distribution is determined continuously or at intervals throughout the experiment.

1) Quasi-Stationary Diffusion Measurements

Techniques falling into this category offer the closest approach to a direct determination of flow where J_1 is computed from the measurement of concentration changes produced in two homogeneous solutions. Since experimental techniques employing solution of Fick's first law offer the easiest approach to measuring diffusion coefficients, a considerable amount of effort has been expended to develop and improve a suitable apparatus. Northrop and Anson (1929) successfully introduced the diaphragm cell technique. In this apparatus diffusion takes place through a porous diaphragm of sintered glass connecting two cells in which the respective liquid concentrations are kept uniform. The diaphragm may be considered to approximate a large number of small parallel tubes. Since the diaphragm has a greatly reduced cross-section, the lessened interfacial area between the two liquids eliminates errors due to thermal or mechanical disturbances. The diaphragm cell technique, as it is most often used today, is based largely on the model designed by Stokes (1950). The Stokes diaphragm cell is illustrated in Figure 1. The diaphragm exhibits an effective cross-section, A, and a path length, l, to the diffusing liquid. In a typical experiment the compartments are

filled with solutions c^1 and c^{11} in such a manner that all the air is forced out of the pores of the diaphragm. Filling the cell with the test solutions requires a strict sequential procedure. Diffusion is allowed to take place until the concentration differences in the compartments are appreciable after which time the cell contents are sampled and diffusion coefficients calculated. D values are evaluated using Equation (4), where c^1 and c^{11} are uniform

$$\ln \left(\frac{c^1-c^{11}}{c^1-c^{11}}\right)_i^f = -\left[\left(\frac{1}{V^1} + \frac{1}{V^{11}}\right)\frac{A}{l}\right]Dt \qquad (4)$$

concentrations on each side of the diaphragm, i and f refer to the initial and final states respectively and t is the time. The cell constant, β, is often evaluated in terms of cell geometry.

$$\beta = \left[(1/V^1) + (1/V^{11})\right] (A/l)$$

β must be determined by calibrating the cell with a material of known diffusion coefficient, for example, urea (Bremer and Cussler, 1970) or potassium chloride (Wedlake and Dullien, 1974).

Equation (4), when applied to the evaluation of D, yields an integral or average diffusion coefficient. If

the differential diffusion coefficient can be considered a linear function of concentration over the concentration range under study and if equal volumes are used on both sides of the diaphragm, the measured integral coefficient is equal to the true differential coefficient for the mean concentrations. However, for systems where D is a function of solute concentration, the conversion of measured integral coefficients into differential coefficients is done mathematically as outlined by Gordon (1945). Often it is desirable to convert integral coefficients into differential coefficients since the latter are more useful as they represent a point condition. Thus they may be used to compare data among different investigators, whereas integral coefficients obtained by different experimental techniques can be compared only qualitatively.

In experiments using the diaphragm cell it is necessary to completely purge the pores of the diaphragm of air or vapor. Entrapment of a gas may seriously alter the effective cross-section for diffusion. There appears to be some uncertainty of the effect that stirring speed has on the experimentally derived diffusion coefficients. As an example, Leffler and Cullinan (1970) state that the cell factor β varied by as much as 12% with stirring speed whereas Ghai and Dullien (1974) state that the stirring

speed does not influence measured diffusivities to any great extent. Equation (4) requires that the logarithm of the ratio of concentration differences be used to calculate D. With small differences in initial concentration, extreme precision is required to reduce the subsequent error in D to a tolerable value because of the multiplying effects of the mathematical treatment. Holmes et al. (1962) studied the diffusion of toluene in various solvents and found that the precision of toluene determinations (as measured spectrophotometrically) was ±1.0%. However, the corresponding error in the diffusion coefficient was ±6%.

Many variations of the original Stokes cell have appeared in the literature. Bremer and Cussler (1970) designed a cell whereby a polarimeter was used to monitor optically active solutes undergoing diffusion. Calus and Tyn (1973) modified the Stokes cell by incorporating a third compartment to accommodate solution expansion occurring at elevated temperatures. Sanni and Hutchison (1973) also designed a cell to work at high temperatures, however, expansion was allowed for by the incorporation of a U-tube containing mercury. Hayduk and Ioakimidis (1976) constructed an apparatus having all the essentials of a diaphragm cell. Their cell was comprised of a cylindrical Teflon disk containing 252 drilled holes each fitted with

a precision stainless steel capillary 2 cm long and 1 mm inside diameter. These authors report that their cell has the advantages of requiring no prior calibration and diffusivities could be measured in relatively short times.

In general diffusion coefficients obtained by the diaphragm cell technique are considered to be accurate to approximately 1%. This technique, however, requires a lengthy time period for significant changes in concentration to occur within the cell components (Holmes et al., 1962). Lees and Sarram (1971) have shown that the diaphragm cell technique may be used close to conditions of infinite dilution as revealed by their study of water diffusivities in organic liquids.

2) Unsteady-State Diffusion Measurements with Analysis at the End of Experiment Only

Capillary cells fall within this category. In the open-ended capillary technique a capillary, which is closed at the bottom and open at the top, is filled with a solution of known concentration. The open end is immersed in a well stirred solvent. Since the volume of the capillary is small compared to that of the solvent, the concentration at the top of the capillary is maintained

close to zero throughout the experiment. At the end of an experiment the diffusion coefficient can be determined by measuring the total amount of material which has passed out of the capillary.

For self-diffusion measurements, particularly when using radioactive materials, the capillary cell has the economic and experimental advantages of requiring only small amounts of diffusing solution (Wang, 1952). With non-radioactive compounds very exacting methods of analysis are required whereas with radioactive materials the isotopic concentration can be determined by adapting the standard techniques for radiation measurement.

Despite diffusion times of up to several days, the capillary technique can provide diffusion coefficients to an accuracy of about 1%. Adamson and Irani (1958) showed, using labelled sucrose, that the diffusion coefficients measured by the diaphragm cell technique and the capillary technique agreed within the limits of experimental error.

3) Unsteady-State Diffusion Measurements with Continuous or Intermittent Analysis

The most desirable method of conducting a diffusion experiment is to use a suitable means of physical

analysis to determine the concentration distribution as a function of time at any desired cross-section of a diffusion cell. Methods for observing concentration changes as diffusion proceeds are then limited only by the accuracy of the analytical method. Although many methods of analysis may be used, for example, electrical capacitance, surface tension, velocity of sound, calibrated floats, absorption of light; only radioactive measurements and refractive index measurements are in common use today.

As with other diffusion techniques, the availability of radioactive isotopes facilitates the measurements of self-diffusion coefficients. Using isotopes emitting beta particles, Walker (1950) determined concentration gradients during diffusion by measuring the activity through a small slit surrounding the diffusion cell. This method is subject to the inaccuracy introduced by a finite slit width and is limited to use with pure beta emitters. This technique, however, allows the utilization of experimental methods that are not feasible with ordinary analytical techniques. One technique that has been used is to continuously measure the amount of material present in a thin layer at the end of a diffusion cell. This is possible if the penetration of the emitted particles is sufficiently small so that only the surface

layer contributes to the observed radioactivity. Beta particles from sulfur-35 and carbon-14 satisfy this condition.

For systems with a suitable difference in refractive index between the two components the measurement of changes in refractive index as diffusion proceeds in a properly designed cell is currently the most reliable way to determine a liquid diffusion coefficient. With most optical techniques the experimental diffusion cell is such that a uniform denser solution is placed beneath a uniform solution of lower density. At the start of the experiment the interface between the two solutions is made as sharp as possible.

Diffusion cells for studying free diffusion must have optically flat, parallel windows and must also be capable of forming a very sharp initial boundary between the two solutions. The Tiselius electrophoresis cell with only slight modification has been found to be the most satisfactory. Kahn and Polson (1947) described a simple capillary sharpening procedure which produced a very sharp initial boundary when adopted to the Tiselius cell. Figure 2 shows the Kahn-Polson cell in which a fine stainless steel capillary produces a sharp boundary between the two solutions. Schachman (1957) thoroughly

discusses the procedures for filling the cell and subsequent boundary formation. Although various other boundary sharpening techniques have recently been developed (Staker and Dunlop, 1973), the diffusion cells used at the present time essentially retain the original Tiselius design.

There are several main methods by which diffusion may be studied using refractive index measurements. These include the schlieren method, the Gouy interference method, the Rayleigh interference method and the Jamin interference method.

English and Dole (1950) measured the diffusion coefficients of sucrose in supersaturated solutions using the schlieren method in conjunction with the Tiselius-type of diffusion cell. The authors found that the schlieren patterns obtained were extremely difficult to interpret. They found that the analysis of the schlieren photographs in different ways gave diffusion coefficients which varied by as much as 12%. Due to difficulties such as these the schlieren method has been largely replaced by interferometric methods. The theory of the schlieren phenomenon is explained well by Gosting (1956) and is elegantly presented in a Beckman publication (1964).

The Gouy interference method owes much of its

success to the efforts of Gosting and co-workers. Studies by these investigators on aqueous solutions of urea (Gosting and Akeley, 1952), glycoamide (Dunlop and Gosting, 1953) and sucrose (Gosting and Morris, 1949 and Akeley and Gosting, 1953) have shown that the Gouy technique is capable of yielding diffusion coefficients accurate to 0.1%. In these experiments which were of approximately four hours duration, diffusion temperatures were constant at ±0.002°C. Sucrose diffusion coefficients obtained by Ellerton and Dunlop (1967) using the Gouy method varied by no more than 0.1% from values previously obtained by Gosting. The theory of the Gouy interferometric technique is discussed by Gosting (1956).

The Rayleigh interference method, the theory of which is also dealt with by Gosting (1956), has been reported to give diffusion coefficients comparable in accuracy to those obtained by the Gouy interferometric method. Thompson and Oncley (1961) calculated a D value for glycine at 25°C with $\bar{c}$ = 0.6101 g/dl from results they obtained at 20°C. Their value of $1.0490 \times 10^{-5} cm^2/s$ compared well with the results of Lyons and Thomas (1950) who obtained a D value of $1.0470 \times 10^{-5} cm^2/s$ using the Gouy method at the same concentration and at 25°C. Glycine diffusion coefficients in water were also measured by

Creeth (1955) using both the Rayleigh and Gouy interferometric techniques which yielded respective values of $1.0451 \times 10^{-5} cm^2/s$ and $1.0458 \times 10^{-5} cm^2/s$.

Chatterjee (1964) using Jamin interference optics found that the diffusion coefficients of sucrose deviated from the values of Gosting and Morris (1949) (Gouy technique) by approximately 0.04%.

There is little doubt that the diffusion coefficients obtained by the various interferometric techniques are by far the most accurate. In many cases diffusion coefficients obtained by interferometric techniques in conjunction with the Tiselius-type diffusion cell are considered as absolute. Inspection of the literature shows that when a new technique for measuring diffusion coefficients is developed or when an older technique is modified, the diffusion coefficients obtained are invariably compared to those obtained from interferometric techniques (Pepela et al., 1970). Diffusion coefficients obtained by interferometric techniques are considered as differential coefficients since the concentration differences employed may be small ($10^{-5} g/ml$).

Recently Chandrasekhar and Hoelscher (1975) reported a study of unsteady-state diffusion of glycerol, glycol and n-butanol in water using the schlieren technique.

Boundary formation was achieved in an analytical ultracentrifuge using a valve-type synthetic boundary cell. Even though the ultracentrifuge has been used for many years to study the diffusion and sedimentation properties of macromolecular species in aqueous solution, the report of Chandrasekhar and Hoelscher (1975) was the first in which the ultracentrifugal technique had been used to investigate the diffusion properties of small molecules in aqueous solution.

Le Maguer et al. (1976) have recently reported measuring diffusion coefficients of small molecules using a preparative ultracentrifuge. The schlieren optical accessory of the ultracentrifuge was converted to 35 mm slr photography (Smyrl et al., 1977).

C. EXPERIMENTAL

1) Chemicals

Diffusing materials included sucrose, glycol and glycine. All were reagent grade and were used as received from the J.T. Baker Chemical Company. All solutions were prepared with distilled-deionized water.

2) Equipment

A Beckman Model L2-65B Preparative Ultracentrifuge (Spinco Division, Beckman Instruments, Inc., Palo Alto, California) was used in the diffusion experiments. The preparative ultracentrifuge was equipped with a schlieren optical accessory (Spinco Division, Beckman

Instruments, Inc., Palo Alto, California) and is described by Griffith and Gropper (1969).

The optical column of the schlieren accessory was modified in such a manner that the photographs of the schlieren image could be recorded by a 35 mm single lens reflex camera rather than the Polaroid camera which was standard with the schlieren accessory. This was accomplished by removing the Polaroid camera from the column and attaching the 35 mm slr camera mount which is depicted in Figure 3. The optical tower of the schlieren attachment for the L2-65B Preparative Ultracentrifuge is represented by A. The tower attachment, B, is mounted on the tower with the existing facilities for the standard Polaroid attachment. The outer edge of B is threaded such that D, the camera adaptor, can screw onto and over B. A double convex lens, C, with a focal length of 20 cm is positioned between B and D. The outerside of B and the inner surface of D are tapered to accomodate the curvature of the double convex lens, C. The camera mount, E, is able to slide horizontally on the barrel of D. The right hand section of the camera mount is threaded to accept a Miranda 35 mm single lens reflex camera body. The camera mount can be securely fastened to D with the tightening nut on the camera mount. During an experiment

in which the schlieren patterns are monitored with time, the light source which is located in the base of the tower is kept illuminated at all times. One preliminary run is required to ascertain the correct camera shutter speed for the light sensitivity of the 35 mm film used. Generally it was found that a shutter speed of 1/8 s was suitable when Tri-X film (400 ASA) was used. To maximize the image sharpness as viewed through the camera viewer, the camera mount was moved horizontally along the barrel of D (Figure 3) and then secured tightly onto D with the tightening nut. Once the correct shutter speed and camera position had been determined no further adjustments were required unless a film of different ASA was used. Following a schlieren pattern with time consisted simply of advancing the film and taking photographs at the desired times.

The diffusion cell was a double sector capillary synthetic boundary cell with a polished Epon centerpiece and quartz windows (Spinco Division, Beckman Instruments, Inc., Palo Alto, California). An Analytical-D rotor (Spinco Division, Beckman Instruments, Inc., Palo Alto, California) was used to house the diffusion cell during the diffusion runs.

A Labline Environmental Chamber (Labline Inc.)

was used to equilibrate the rotor, cell and solutions at the required temperatures. Chamber temperatures are accurate to ±0.2°C. Magnification of schlieren images on 35 mm negatives was accomplished with a Kodak Ektagraphic Slide Projector, Model AF (Kodak).

3) Methods

Sucrose and glycine were prepared on a weight-by-volume basis whereas the glycol solutions were prepared on a weight-by-weight basis. All solutions were used on the same day of preparation to avoid effects of microbial growth. After cell assembly, the left hand sector of the cell was completely filled with the less dense solution. The right hand sector was flushed twice with the more dense solution and was then filled with the more dense solution such that the top of the meniscus just reached the lower capillary (0.15 ml). For all aqueous solutions used in this study, the density was found to increase with increasing solute concentration. To avoid possible leakage from one sector to another, through either the top or bottom capillary, the cell was kept in a horizontal position until the time of the diffusion run. For runs at 25°C the chamber of the preparative ultracentrifuge was prewarmed with a goose-

necked lamp. This step was necessary since the Model L2-65B was not equipt with a chamber heating system and the surrounding laboratory temperature was usually less than 25°C. For diffusion runs at 25°C, the rotor, cell and solutions were equilibrated for at least 1 h at 25°C. For runs below room temperature the chamber was precooled using the refrigeration unit of the L2-65B, and the rotor, cell and solutions were precooled to the desired temperature in the Labline Environmental Chamber. After the rotor containing the cell was placed on the driveshaft of the centrifuge the chamber door was closed and the chamber was evacuated. When the chamber pressure had reached 200 μ the rotor was accelerated to the desired final revolutions per minute. As the rotor begins to accelerate the less dense solution in the left sector flows through the lower capillary of the diffusion cell and layers onto the more dense solution in the right sector. The less dense solution was layered onto the more dense solution to maintain gravitational stability (Gosting and Fujita, 1957).

Photography of the schlieren patterns in a diffusion run was initiated after the position of the air-liquid interface in the right sector had stabilized. The time intervals between successive photographs depended

on the diffusion rate of the particular compound being studied. For example, during sucrose diffusion runs, 1 min time intervals between successive photographs were found to be suitable. For glycol studies a time interval of 30 s was used. In all diffusion runs photographs were taken until the peak height had decreased to approximately 50% of the height of the first photograph. The angle of inclination of the schlieren diaphragm θ was selected so that an optimum in peak height and peak sharpness was obtained.

After a diffusion experiment, the film was removed from the camera and developed according to specifications outlined by the manufacturer of the film. The 35 mm negatives were mounted in 35 mm glass slide mounts. Glass slide mounts were necessary to prevent any bulging of the negative. The Kodak slide projector was then used to project the schlieren images onto a vertical gradient such that the peak height was magnified by a factor of approximately 40X. The projector was adjusted so that the base line of the vertical gradient bisected the baseline of the schlieren image. The projected schlieren image was horizontally shifted so that the schlieren peak maximum coincided with X=0 on the vertical gradient. Once the schlieren peak was properly aligned

on the vertical gradient, the height of the peak was measured at 5 mm intervals (X=0, ±5, ..., ±35 mm). Peak heights were measured from the middle of the base line to a point corresponding to one half the vertical thickness of the peak image at each value of X. The reference lines arising from the counterbalance in the Analytical-D rotor were used to calculate the magnification factor β. A value of β was determined from each photograph in the diffusion experiment and an average value of β was used to calculate the diffusion coefficient for that particular run.

Diffusion coefficients were calculated using a linear regression involving Equation (5). The derivation

$$\ln(y' t^{\frac{1}{2}}) = \ln\left(\frac{\alpha \Delta c}{2\sqrt{\pi D}}\right) - \frac{x'^2}{\beta^2 4Dt} \qquad (5)$$

and notation of Equation (5) are outlined in Appendix A1. Appendix A2 describes the computer program used to calculate the diffusion coefficient. Since fifteen values of y' and x' were obtained from each photograph and since at least five photographs were taken during the diffusion run, the resulting D value was calculated from a linear regression involving at least 75 points.

Zero time corrections (Longsworth, 1947) were determined using the method outlined by Chervenka (1969). The zero time corrections were incorporated into all calculated diffusion coefficients.

All diffusion experiments were conducted in triplicate.

D. RESULTS

The diffusion coefficient of sucrose was determined as a function of average sucrose concentration. In these experiments, conducted at 25.3°C, the average sucrose concentration, $\bar{c}((c_1+c_2)/2)$, was systematically varied from values of 1.000g/100ml to 7.000g/100ml. The concentration difference, $\Delta c(c_1-c_2)$, was kept constant at 2.000g/100ml. Δc values of this magnitude were chosen because previous investigators (Gosting and Morris, 1949 and Chatterjee, 1964) had shown that the diffusion coefficients of sucrose are independent of Δc values in this range. Moreover, Gosting and Morris (1949) state that the variation of the refractive index with concentration is linear over the concentration range studied in this work. Hence these experiments are considered to yield the differential diffusion coefficient corresponding to the mean concentration.

Figure 4 shows a plot of the experimentally determined sucrose diffusion coefficients as a function of $\bar{c}$, □. The least square line relating D with $\bar{c}$ is given by Equation (6). The least squares analysis

$$D = 5.32(1-0.0138\bar{c}) \times 10^{-10} \qquad (6)$$

yielded a correlation coefficient of -0.993 indicating an excellent linear relationship between D and $\bar{c}$. The interferometrically obtained results of Gosting and Morris (1949) at a slightly lower temperature of 24.95±0.005°C are also included in Figure (4), O. The least-square line relating D to $\bar{c}$ as applied to the data of Gosting and Morris (1949) is given by Equation (7). The least-square analysis as applied to the data

$$D = 5.226(1-0.0148\bar{c}) \times 10^{-10} \qquad (7)$$

obtained with the ultracentrifugal technique and the absolute data of Gosting and Morris (1949) show that the slopes are within 5% of each other. The slope of the D vs. $\bar{c}$ plot may be considered as a criterion for assessing the sensitivity of D to $\bar{c}$. Thus it appears that the ultracentrifugal technique is sufficiently sensitive to

monitor the variation of the diffusion coefficient with small changes in the average concentration of the diffusing molecule.

From Equations (6) and (7), the values of the diffusion coefficient at infinite dilution, D^0, are $5.32 \times 10^{-10} m^2/s$ and $5.226 \times 10^{-10} m^2/s$ respectively. The slightly higher D^0 value from the ultracentrifugal technique over that obtained using Gouy interferometry is expected because of different experimental temperatures. Using the well known Stokes-Einstein relationship, as depicted in Equation (8), and available viscosity data

$$D_0 N_0 / T = D_0^1 N_0^1 / T^1 \qquad (8)$$

for water (Handbook of Chemistry and Physics, 1969), the value of D^0 from the ultracentrifugal technique becomes $5.27 \times 10^{-10} m^2/s$ at 24.95°C. This represents a 1% deviation from the absolute value of Gosting and Morris (1949). The D^0 obtained by the ultracentrifugal technique also compares well with the results of Chatterjee (1964) who measured a D^0 value of $5.224 \times 10^{-10} m^2/s$ using the Jamin interferometric technique.

Table 1 shows the diffusion coefficients of sucrose at 25.0°C as a function of final rpm setting on

the ultracentrifuge. In these experiments $\bar{c}$ and Δc were kept constant at 1.000g/100ml and 2.000g/100ml respectively. The Dav values listed in the third column of Table 1 show that the diffusion coefficients are independent of rpm over the range studied. Calculation of an overall average diffusion coefficient Davo, yields a value of $5.19 \pm 0.05 \times 10^{-10} m^2/s$ whereas Gosting and Morris (1949) found a value of $5.148 \times 10^{-10} m^2/s$ at 24.95±0.005°C with $\bar{c}$ = 1.011g/100ml and Δc = 1.5016g/100ml. Table 1 also serves to point out that the experimentally determined diffusion coefficients are precise to approximately 1% (as measured by the relative standard deviation).

Table 2 illustrates the variation of sucrose diffusion coefficients with temperature where $\bar{c}$ and Δc have been kept constant at 1.000g/100ml and 2.000g/100ml respectively. Again the results of Gosting and Morris (1949) are included for comparative purposes. Dlit values for T=2.6 and 14.8°C have been calculated from the respective data of Gosting and Morris (1949) at 1.00 and 24.95°C, hence they should be considered as approximate. Again the precision of the experimentally determined diffusion coefficients is good in all cases. A plot of ln(Dexp) vs. 1/T(°K) (Glasstone et al., 1941)

follows the expected linear relationship as evidenced in Figure 5, and thus would permit determination of activation energies of diffusion. Thus the ultracentrifugal technique of determining diffusion coefficients appears useful in temperature related investigations.

The ultracentrifugal technique was extended to the study of ethylene glycol in water. Diffusion coefficients were determined at 25.0°C using several $\bar{c}$ values as shown in Table 3. The least square line relating Dexp and $\bar{c}$ renders a D° value of $1.14 \times 10^{-9} m^2/s$ which compares well with D° = $1.16 \times 10^{-9} m^2/s$ as obtained by Garner and Marchant (1961) who used the interferometric technique. A least squares analysis of the data presented by Byers and King (1966) yields a D° value of $1.17 \times 10^{-9} m^2/s$. However, inspection of Figure 6, which includes data from this study, □, and data presented by Byers and King (1966), O, shows that the diffusion coefficients obtained by the ultracentrifugal technique are consistently below the values of Byers and King (1966) who used the diaphragm cell technique. Moreover, the plots representing the different data appear to diverge towards increasing ethylene glycol concentrations.

The diffusion coefficients of glycine in water at 25.0°C ($\bar{c}$ = 0.5995g/100ml and Δc = 1.990g/100ml) was

found to be $1.02\pm0.01\times10^{-9}m^2/s$. This result compares favorably with Thompson and Oncley's (1961) value of $1.049\times10^{-9}m^2/s$ at 25.00°C. Creeth (1955) obtained values of $1.0451\times10^{-9}m^2/s$ and $1.0458\times10^{-9}m^2/s$ using the Rayleigh and Gouy techniques.

E. DISCUSSION

1) Importance of an Initially Sharp Boundary

Diffusion coefficients, obtained by the ultracentrifugal technique, have been determined using Equation (5) which is essentially an integrated form of Fick's second law (Equation (2)). When Fick's second law is integrated, the following initial and boundary conditions are required. c_1 and c_2 represent initial

$t=0$	$t>0$
$c=c_1 \quad (x<0)$	$c\rightarrow c_1 \quad (x\rightarrow-\infty)$
$c=c_2 \quad (x>0)$	$c\rightarrow c_2 \quad (x\rightarrow\infty)$

solute concentrations on each side of the boundary which is located at x. Longsworth (1945) showed that integration of Equation (2) yields the following relation.

$$\frac{\partial c}{\partial x} = \frac{\Delta c}{2\sqrt{\pi Dt}} e^{-x^2/4Dt} \qquad (9)$$

In a two component system where the refractive index, n, is a linear function of the solute concentration, n may be substituted into Equation (9) to give Equation (10).

$$\frac{\partial n}{\partial x} = \frac{\Delta n}{2\sqrt{\pi Dt}} e^{-x^2/4Dt} \qquad (10)$$

The schlieren optical system of the preparative ultracentrifuge used in this study records the variation of $\partial n/\partial x$ with x in the diffusion cell.

Figure 7 illustrates a theoretical diffusion process in which solutions of concentration c_1 and c_2 have been brought together to form a perfectly sharp interface at t=0 and at a position x=0 in the diffusion cell. The first vertical set of diagrams represents the concentration profile curves with concentration increasing along the vertical axis and distance within the diffusion cell represented by the horizontal axis. To the right are the corresponding concentration gradient curves as would be produced by the schlieren optical system. These schlieren curves are recorded by the 35 mm

camera and it is from these curves that x^1 and y^1 are measured.

Assuming a very sharp interface at t=0, the concentration profile curve takes the form of a step curve with the concentration to the left of x being c_1 and the concentration to the right of x equalling c_2. Under these conditions the requirements for integration of Fick's second law are fully satisfied. At times greater than t=o there will be a net flux of solute molecules from the region of higher concentration, c_2, to the region of lower concentration c_1. This net flux of the solute molecules is the diffusion process. The molecules of solute closest to the interface in the c_2 region (x>0) will be the first to cross the interface into the c_1 region. Therefore the solute concentration to the right of x will decrease near x and correspondingly the solute concentration in the c_1 area (x<0) very near to x will increase. The resulting concentration profile diagram from the initial diffusion is represented by the t=100 s case. The boundary region between c_1 and c_2 in this case is very narrow, that is, the concentration varies by a large amount over a short distance along x. Thus the resulting concentration gradient curve is sharp and narrow. As time passes the width of the boundary

increases and the rate of change of concentration with x diminishes. Consequently the corresponding concentration gradient curves broaden and decrease in intensity as shown in the t=200 s and t=300 s cases. A time will be reached when the concentrations of the solute at the cell extremities begins to vary. When this happens the diffusion experiment has reached a stage of restricted diffusion and the calculation of diffusion coefficients according to Equation (5) is no longer valid. At $t=\infty$ the solution is homogeneous.

Figure 8 shows the actual schlieren peaks as recorded on 35 mm film. These photographs represent a sucrose diffusion experiment at 25°C ($\bar{c}$ = 1.000g/100ml and Δc = 2.000g/100ml). The peak height is seen to decrease with time and the peak width increases with increasing time. This peak behavior is in accordance with the previously discussed theoretical diffusion experiment.

Figure 9 (a, b, c and d) illustrates how the photographically obtained schlieren image is influenced by the bar angle (θ) setting of the schlieren optical system. These photographs were recorded within seconds of each other hence they represent the concentration gradient curve at the same time. Comparison of Figure 9a

(θ=75°) and Figure 9b (θ=80°) show that as the bar angle is increased the schlieren image becomes sharper but the peak height decreases. At bar angles of 60° and 50°, as shown in Figures 9c and 9d respectively, the peak height is greatly enlarged but clarity and sharpness are sacrificed. Therefore the choice of which bar angle is used in an experiment is based upon which bar angle will give the highest degree of precision when y^1 values are measured. The precision of measured y^1 values will be a function of both image height and sharpness.

The mathematical derivation of Equation (5), as discussed previously, is based on the assumption that at t=0 a perfectly sharp interface is present between the two solutions. Therefore it is essential that the boundary between the two solutions be as sharp as possible and it is this requirement that has prompted much research towards better boundary formation techniques especially with the interferometric-Tiselius cell methods.

Currently there are several centerpieces available which can accomplish boundary formation between two solutions in an ultracentrifuge. The valve-type synthetic boundary cell and the double sector capillary

synthetic boundary cell are illustrated in Figure 10. Both devices operate on the principle that the less dense solution is layered on top of the more dense solution under the influence of a gravitational field. Chandrasekhar and Hoelscher (1975) used the valve-type synthetic boundary cell in their ultracentrifugal determinations of the diffusion coefficients of n-butanol, glycerol and ethylene glycol. The valve-type cell contains a small rubber valve which is compressed as the rotor speed increases. When the valve is fully compressed the less dense solution present in the cup is allowed to drain into the wedge-shaped sector containing the more dense solution. Earlier work in this laboratory with this type of cell revealed that a considerable amount of turbulence occurred at the interface of the two solutions as boundary formation was taking place. This turbulence was monitored by photographing the schlieren image as the liquid from the cup was being layered onto the liquid in the sector. Figure 11 (a, b and c) shows successive photographs taken during boundary formation in the valve-type cell. It is obvious that considerable mixing occurs as the schlieren peaks exhibit definite irregularities which are most evident at the base of the peaks. Figure 11d illustrates the resultant peak after boundary for-

mation has ceased. The peak appears to be far from symmetrical as would be expected if the diffusion were to commence from an initially sharp interface. This turbulence during boundary formation probably results from the momentum acquired by the less dense solution as it falls from the cup to the layer of more dense solution already present in the body of the cell. The result is a distorted schlieren peak and apparently erroneous diffusion coefficients (Huang and Winnick, 1976).

In this study the double sector capillary synthetic boundary cell (Figure 10) was used as the diffusion cell. With this type of cell the less dense solution flows from the full sector to the sector partially filled with the more dense solution. Figure 12 illustrates the mechanism of boundary formation in this cell. As the rotor gains speed the less dense solution is forced through the lower capillary onto the more dense solution. Since the surface of the more dense solution is level with the lower capillary, boundary formation is achieved without the less dense solution having to fall through any appreciable distance before contacting the more dense solution. The less dense solution will flow into the opposite sector until the levels in both sectors are equal. The upper capillary serves the purpose of

allowing the air in the sector being filled to flow into the sector being emptied. An additional feature of the double sector capillary synthetic boundary cell is that as the less dense solution enters the lower sector it sweeps over the interface and thus sharpens the boundary.

Boundary formation with the double sector capillary synthetic boundary cell was investigated photographically. Figure 13 (a to g) shows the schlieren images recorded at 15 s intervals starting from the time of rotor acceleration. It is evident that none of the irregularities, which were observed in photographs of boundary formation with the valve-type cell, are present in Figure 13. The resultant schlieren peaks appear very symmetrical as shown in Figure 13h. Analysis of enlarged schlieren peaks reveal that they do indeed approach the shape of a Gaussian curve. Further evidence of sharp boundary formation lies in the fact that the calculated zero time corrections, Δt, are invariably in the order of a few seconds.

2) Calculation of the Diffusion Coefficient

Neurath (1942) has described several standard methods to calculate diffusion coefficients from schlieren photographs of diffusing systems. The maximum ordinate

method involves dividing the maximum ordinate, h max, by e to give the ordinate of the inflection points, hμ. The diffusion coefficient is calculated by the relation, $D = \mu^2/2t$ where μ is one half the distance between the inflection points. Thus the diffusion coefficient is based on a single peak measurement from a single photograph. In the method of successive analysis the diffusion curve is divided into a series of vertical and horizontal chords and the diffusion coefficient is calculated from a pair of successive values of x_i and y_i. Thus the diffusion coefficient is calculated from two height measurements on a single photograph.

The frequently used maximum height-area method of calculating diffusion coefficients was used by Chandrasekhar and Hoelscher (1975) and English and Dole (1950). This type of analysis involves a plot of $(h_i max)^2$ vs. $1/t_i$ from which the diffusion coefficient is calculated from the slope. A knowledge of the peak area is also required. Such plots appear to yield excellent linear relationships. However, as pointed out by English and Dole (1950), there is uncertainty in the absolute magnitude of the diffusion coefficient because considerable personal latitude exists in estimating both peak height and peak area. Since peak height

determinations are limited to an accuracy of about 1% (Gosting, 1956), the diffusion coefficients calculated by the technique cannot be expected to give results with a precision better than 4% (the maximum height-area method involves the square of the peak height and the square of the peak area).

When Equation (5) is used to determine diffusion coefficients from schlieren peaks, the only error involved is that incurred in measuring the peak height, y^1, at various values of x^1. Use of Equation (5) also avoids the necessity of determining the peak area (which includes a $(h^1max)^2$ term) thus eliminating any uncertainty in the diffusion coefficient arising from this quantity. Since peak heights, y^1, are measured at fifteen values of x^1 on each peak and since at least five peaks are recorded during a diffusion experiment, the resulting diffusion coefficient is based on at least 75 y^1 values. Diffusion coefficients calculated by the maximum height-area method are typically based on a plot consisting of five to ten points. Figure 14 illustrates a plot of Equation (5) for glycine at 25.0°C.

3) Adaptation of the Schlieren Optical System to 35 mm Photography

Conversion of the schlieren optical attachment of the Beckman Model L2-65B Preparative Ultracentrifuge to 35 mm photography offers several advantages to the measurement of diffusion coefficients of small molecules. With the Polaroid attachment which is standard with the schlieren accessory, the time of exposure of the film to the light is regulated by switching the light source on and off. When double sector cells are used, a period of up to 10 s exposure time may be required when the Polaroid-type of film is used (Beckman, 1969). Exposure times of this duration do not yield sharp photographic images of a rapidly changing schlieren pattern. The height of a schlieren peak may decrease by five percent in such a 10 s time period as has been evidenced in the diffusion of small molecules. However, when a high speed film is used with the 35 mm adaptation, very short exposure times are required and very sharp images are recorded.

Generally, measurements on the photographic images of optical patterns formed in an ultracentrifuge are performed with an optical microcomparator (Chervenka, 1969) or analogously on tracings of the optical pattern made under an enlarger. According to Schachman (1957)

the measurement of schlieren patterns which have been enlarged by a factor of five is comparable to using a microcomparator. Since very clear and sharp images are obtained with the 35 mm system, magnification to 40X yields high clarity enlargements. Hence the magnitude of relative error on image measurements is minimized.

The 35 mm adaptation offers several other advantages not attainable with the standard polaroid attachment. The ability of the apparatus to take pictures at intervals of several seconds is essential when measuring diffusion coefficients of small molecules since they diffuse very rapidly. The investigation of boundary formation in the valve-type and double sector capillary synthetic boundary cells would not have been possible with the Polaroid camera. The adaptation to 35 mm slr photography offers the convenience of being able to simultaneously observe and record schlieren images. Such a feature as constant viewing is useful, for example, to insure that schlieren peaks are not recorded when the point of restricted diffusion is reached. With the unmodified system, if further viewing is desired once the Polaroid camera is installed, the camera must be removed and replaced with the viewing apparatus. Because of the fact that high clarity enlargements may be produced,

the 35 mm adaptation lends itself to the study of phenomena occurring in a very narrow range about the interface. In sucrose diffusion experiments, it has been determined that the actual physical size of the concentration gradient is less than 1.5 mm.

Figure 15 summarizes the comparison between diffusion coefficients obtained by using interference optics (ordinate) and diffusion coefficients arising from the other methods (abscissa). The closeness of the ultracentrifugally determined diffusion coefficients to the 45 degree line asserts their validity and reflects the substantial improvement in the accuracy of the ultracentrifugal technique compared to previous work with an analytical ultracentrifuge (Chandrasekhar and Hoelscher, 1975). The dashed lines in Figure 15 represent the limits of the 5% deviation interval. It must be emphasized at this point that the ultracentrifugal technique involves an experiment of less than 10 min duration whereas interferometric or diaphragm cell techniques involve times of hours or even days.

4) Possible Extensions of the Ultracentrifugal Technique

It is conceivable that this ultracentrifugal technique could be extended to yield diffusion coefficients

of increased accuracy and precision. The Beckman Model E Analytical Ultracentrifuge has a much better temperature control (±0.05°C) than the Model L2-65B used in this study and would allow for diffusion studies at elevated temperatures. In addition the Model E is equipt with a Rayleigh interference optical system. Besides yielding more accurate diffusion coefficients, the Rayleigh system would permit diffusion studies at concentration levels well below those possible with the schlieren optical system.

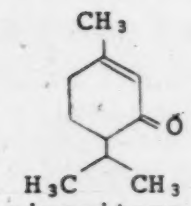
II. Retention of Essential Oil Components During Freeze Drying of Aqueous Solutions

A. INTRODUCTION

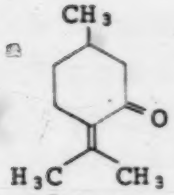
Freeze drying may be defined as a low temperature dehydration process. At low partial pressures of water and at low temperature, the water is removed from the frozen product by sublimation. The key to the success of freeze drying in producing high quality products such as instant coffee, fruit juices and instant tea (Flink, 1975a) lies both in the removal of water by sublimation as well as by the low temperatures employed. Since the material undergoing dehydration by the freeze drying technique is normally in a frozen or rigid state, the matrix remaining after the disappearance of the ice crystals essentially remains intact. Thus the freeze-dried products rehydrate completely and quickly. Spillage losses during processing which may occur as a result of frothing or bubbling are eliminated since a free liquid phase is not present. Redistribution of soluble components by capillary flow is limited due to the absence of a free liquid phase. In a freeze drying sample, the transition zone separating the fully hydrated frozen product and the dry layer is very sharp, hence the

time is short where any portion of the product is kept in an intermediate moisture state where undesirable degradative reactions might occur. As pointed out by King (1971), the lower temperatures employed will cause the dehydration rate to decrease. However, at lower temperatures the rate of undesirable degradative reactions, such as non-enzymatic browning, is decreased to a much greater extent. Low temperatures also provide a favorable environment for biological molecules such as proteins.

This study is concerned with the retention of terpenic (carvone, piperitone and pulegone) and non-terpenic (eugenol and m-anisaldehyde) essential oil components in model aqueous systems during freeze drying. The essential oil components used in this investigation are commonly found in many food systems. Table 4 has been prepared from the review of Hall and Oser (1965). The amounts listed as "average maximum parts per million" are not tolerance limits and are often exceeded in use. The dissolved solids used in preparing the model systems include sucrose, glucose, gum arabic and sodium chloride which are all common food components.



piperitone



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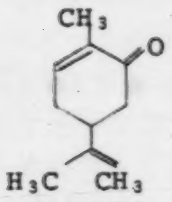
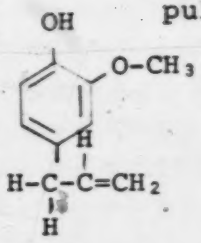
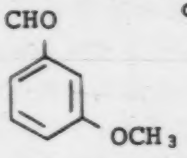


carvone



eugenol



m-anisaldehyde

B. LITERATURE REVIEW

Many excellent review articles dealing with various aspects of freeze drying are available. King (1970) has reviewed many of the fundamental areas of the process and discusses possible degradative reactions which may take place in the dried product. The publication of the lectures from the "International Course on Freeze Drying and Advanced Food Technology" held in Bürgenstock, Switzerland in June 1973 provides an excellent review of many areas of freeze drying (Goldblith et al., 1975).

Since the present study deals with the retention of volatile flavoring compounds in aqueous solutions during freeze drying, the literature review will first of all be concerned with the freezing and

subsequent drying of aqueous solutions. The retention of volatile organic compounds, as influenced by various freeze drying parameters, will then be discussed.

1) Freezing of Aqueous Solutions

The behavior of a solution during freezing depends to a large extent on the composition of the dissolved solute. Several studies have shown that, for example, salt solutions freeze very differently than carbohydrate containing solutions. Using a macroscopic observation technique, Ito (1970a, b) has shown that solutions of sodium chloride, potassium chloride and sodium hydroxide form well defined eutectics. Ito (1970a, b) attributed the formation of densely opaque spots in the freezing salt solution to the formation of the eutectic structure. The temperature at which these macroscopic changes occurred was the eutectic temperature, T_e, and these eutectic points were confirmed by electrical resistance measurements. However, for solutions containing glucose, sucrose, lactose and other sugars no or very little macroscopic change in appearance was observable. Electrical resistance measurements also failed to produce evidence of any type of eutectic transition.

During the freezing of aqueous solutions, an increased separation of pure ice occurs with decreasing temperature and the remaining solution is thereby concentrated. The concentration of the residual solution changes according to the ideal relationship between the equilibrium freezing curve and the concentration. Hence the concentration of the residual solution may accurately be expressed as a function of temperature. The principles governing this phenomenon are explained by Heiss and Schachinger (1951).

According to Bellows and King (1973), when solutions are cooled to very low temperatures, nucleation of solutes other than ice and salts is very difficult since the latter solidify completely at the eutectic point. Food liquids such as juices or extracts contain dissolved solutes (carbohydrates) which are not able to solidify at the eutectic point. Figure 16 illustrates the phase diagram for the sucrose-water system. If equilibrium prevails for both sugar and water, the sucrose-water system should solidify completely at -13°C, the eutectic temperature. However in practice these solutions do not form any crystallized sugar and thus do not solidify completely at temperatures well below -13°C. Instead the observed behavior follows the exten-

sion of the ice-equilibrium curve which represents equal chemical potential between ice and water remaining dissolved in the concentrated solution. Thus the initial liquid separates into two equilibrium phases consisting of solid pure ice and a region of concentrated solutes. This concentrated region has been labelled the concentrated amorphous solution, CAS, since it has no long range ordered structure. Figure 17 diagramatically illustrates the two equilibrium phases in the frozen product. In reality the actual structure is much less regular than that presented in Figure 17.

Within the volume occupied by the CAS, Massaldi and King (1974a) have shown that a concentration polarization phenomenon occurs near the face of the growing crystal. Ice crystals form very selectively, rejecting dissolved solutes and suspended matter away from the growing crystal structure. These rejected substances must diffuse away from the crystal surface or else they will accumulate near the surface of the ice crystal. However, under conditions of low temperature and elevated concentrations which are prevalent during freezing, diffusion of the rejected substances away from the ice is hindered. Dissolved solute or suspended matter concentrations will consequently attain

levels higher at the outer extremeties of the CAS region than concentration levels in the interior portion of the CAS. The concentration polarization is depicted in Figure 18. The solute concentration at the ice surface corresponds to equilibrium with the ice at the prevailing temperature, therefore for a low enough diffusivity this phenomenon will stop ice crystal growth. The polarization theory finds support from observations that show there is a limiting initial dissolved solids content above which no ice-crystal formation will occur at all.

Studies on the physical nature of the CAS network have been carried out by Bellows and King (1973) and as will be discussed later, the fluidity of the CAS is of primary importance. Viscosity measurements of sugar solutions at temperatures and concentrations approaching those expected of the CAS have shown that the CAS is highly viscous and can be considered rigid below a critical temperature.

Several studies have shown that during the freezing of aqueous solutions, an impermeable film may be formed on the outer surface of the product. Ito (1970b) reported that during the freezing of a 10% ε-amino caproic acid solution, a shell is produced on

the surface which has a solute concentration approximately 5X that of the bulk. Quast and Karel (1968) found that during the freezing of liquid extracts a concentrated region of solute developed at the free surface and attributed this to the concentration of carbohydrates. The same behavior has been noted during freezing of whole egg concentrates where the lipid and protein fractions concentrate at the surface (Flink and Fosbol, as reported by Flink, 1975a). Ito (1970b) and Bellows and King (1973) have attributed this phenomenon to the concentrated solutes region being pushed upward through the growing ice crystals as freezing proceeds. Thus the solute is more concentrated in the surface layer than in the bulk and in the highly concentrated layer, nucleation and crystal growth will be minimized as discussed previously. Flink (1975a) has outlined several methods for preventing or eliminating this surface layer formation as it has a detrimental influence on the subsequent drying process.

In many liquid foods a second liquid phase may be present before freezing or may be formed during the freezing process. Often this immiscible phase may be a flavoring substance such as d-limonene (Massaldi and King, 1974b, c). In the case of d-limonene, the compound

is initially present at levels which exceed the solubility limit in aqueous solution. Massaldi and King (1974a) speculate that the components of the second phase may be distributed in three ways during freezing; volatile droplets present at the CAS-ice interface, volatile droplets embedded in the CAS and volatile molecules homogeneously dissolved in the CAS. Furthermore Massaldi and King (1974a) postulate that volatiles which are in homogeneous solution prior to freezing remain in solution within the CAS and do not develop into droplets under conditions of low temperature and high concentrations within the CAS. The authors suggest that the volatile components undergo a similar concentration polarization as dissolved solids and for exactly the same reason (Figure 19).

Flink et al. (1973), using microscopic techniques, have studied aqueous solutions of maltodextrin and hexanol during freezing. In contrast to the view of Massaldi and King (1974a), these authors suggest that during the freezing process, the hexanol (volatile) solubility limit is exceeded as evidenced by the appearance of many droplets. The droplets are then entrapped in the interstitial solute matrix of maltodextrin. Of particular interest is the fact that hexanol droplet

formation occurs over a wide range of initial volatile concentrations. The appearance of liquid droplets of alcohols in freeze-dried aqueous maltodextrin solutions was related to the solubility of the volatile alcohols (Flink and Gejl-Hansen, 1972). Massaldi and King (1974a) photographed sucrose solutions containing the insoluble compounds n-hexyl acetate and d-limonene and concluded that drop size increases with increasing amounts of the volatiles in excess of their saturation concentration.

The morphological structure of the frozen product is strongly influenced by the rate at which the solution is frozen. Thijssen and Rulkens (1969) have shown that a decrease in freezing rate results in an increase of the width of the ice region and correspondingly results in an increase in the thickness of the CAS regions as represented in Figure 17.

2) Drying of Frozen Aqueous Solutions

The drying of a frozen aqueous solution may be considered as a two stage process. The first step involves the removal of pure ice from the frozen material by sublimation. The second step is the removal of water from the CAS region by evaporation. The drying

process is governed mainly by the mass transfer of water vapor which in turn is regulated by the heat provided to the ice within the frozen sample. The balance between heat and mass transfer determines the drying rate. The parameters influencing these transfers have been reviewed by King (1970), Karel (1975) and Rothmayr (1975). In general it has been shown that the properties of the dry layer have an important influence on heat and mass transfer. The freezing rate also has an ultimate effect on drying due to its influence in regulating pore size and the resulting loss of water vapor.

The drying rate and the quality of the product are influenced by the structure of the frozen product. Ideally during the removal of water, the structure of the product is retained if proper conditions are maintained throughout the drying process. However, if structural changes do occur during drying, vapor transfer from the sample may be retarded. Depending on the nature of the frozen product, i.e. eutectic forming or non-eutectic forming, different theories have been advanced to describe structural changes which could occur during drying.

For solutions of sodium chloride and potassium

chloride which form well defined eutectics during freezing, the shaded portions of Figure 17 would represent the eutectic mixture. During sublimation, ice in the eutectic mixture would sublime soon after passage of the ice front, leaving behind a matrix of dry crystalline solute. Collapse, or loss of structural integrity of the frozen sample, will occur at the collapse temperature, Tc. When the frozen zone temperature exceeds T_c the rigid eutectic mixture would redissolve to a liquid. This liquid, under the influence of surface tension and gravitational forces, would flow and seal the open pores left by the sublimed ice. This collapse phenomenon, termed the eutectic melting theory of collapse, may be envisioned as a series of progressive steps as illustrated in Figure 20. For eutectic forming solutes Ito (1970b) has demonstrated that the collapse temperature, $T_{c'}$ is equivalent to T_e. As Figure 20 illustrates, the pores through which water vapor must flow away from the ice front are blocked. Consequently collapse results in a lower drying rate.

Ito (1970a) and Bellows and King (1973) have discussed collapse in drying systems which do not form a eutectic. The latter authors have labelled such collapse "the amorphous viscosity theory of collapse". In this case the shaded portion of Figure 17 represents the CAS region.

After passage of the ice front collapse occurs if this interstitial concentrate does not remain sufficiently rigid to maintain its structural integrity. If rigidity is not maintained the concentrate region will develop liquid tendancies and flow, thereby closing the pores above the ice front. Again Figure 20 represents the progressive steps of collapse. Sealing of the pores causes puffing and splattering as water vapor bursts through this liquid barrier which separates the region of elevated water partial pressure immediately above the ice front from the region of lower vapor partial pressure as determined by the condenser temperature of the freeze drier. Since collapse reduces the permeability of the dry layer to the flow of vapor, the drying rate will decrease. As a result, the requirements for the heat of sublimation will decrease causing the temperature of the frozen zone to rise. Consequently the fluidity of the residual concentrate increases and accentuates the tendancy toward collapse. The vital factor determining whether collapse occurs or not is the viscosity of the concentrate, which in turn is a function of both concentrate temperature and concentrate composition. Bellows and King (1973) have calculated that during a normal freeze drying experiment collapse occurs when the viscosity of the concentrate falls

within the range of 10^7-10^{10} cP. Viscosity measurements and collapse studies by these workers supported the calculated limits of collapse viscosity. Swinnen et al. (1976), however, found that collapse occurs when the critical viscosity zone is situated between 10^5 and 10^7 cP.

In addition Swinnen et al. (1976) have correlated the temperatures at which collapse occurs with the devitrification temperature. The devitrification temperature is defined as the temperature at which the CAS molecules acquire sufficient mobility to pass from the amorphous to the crystalline state. Ito (1971) and MacKenzie (1975) had reported similar correlations.

Bellows and King (1973) have discussed the effects that parameters such as solute composition, solute concentration, the presence or absence of a surface layer and the type of heat transfer geometry have on collapse temperature.

As discussed previously, solute migration during freezing produces a layer of high solids content on the surface of the frozen product. Such a surface layer may block the vacant pores remaining after the ice has sublimed. Consequently the drying rate will be decreased and to prevent collapse, lower drying tem-

peratures are required.

Microscopic investigations of the freeze-drying process have recently come into prominence. MacKenzie (1965) studied the possible paths followed by water vapor during dehydration. Flink et al. (1973) have photographed freeze-dried maltodextrin solutions. Gejl-Hansen and Flink (1976) have applied optical and electron microscopic techniques to the study of structures of various freeze-dried foods.

At this point it is appropriate to mention that structured foods can be dried at much higher temperatures than liquid systems owing to the fact that the structure of the food gives support to the frozen fluid part.

3) Volatile Retention During Freeze Drying; Freeze Drying Parameters

The concentration of volatile flavoring compounds in a rehydrated freeze-dried food should be very close to their concentration prior to freeze drying if the product is to be organoleptically acceptable. Due to their low concentrations in aqueous solutions nearly all flavoring components, even the high boiling ones, are much more volatile than water. With elevated volatilities such volatiles would be lost in an evaporation

process (Rulkens and Thijssen, 1972b). Chandrasekaran and King (1971) showed that the retention of volatile compounds, during the freeze drying of fruit juices, was independent of their relative volatility. Similarly Flink and Karel (1970a, 1970b) and Karel and Flink (1973) were not able to find any direct correlation between the volatility and the degree of retention of volatile compounds during freeze drying. However, Voilley et al. (1973), Saravocos and Moyer (1968) and Chalmers and Watts (1972) reported that in their studies the degree of volatile retention was influenced by the volatility of the volatile compound.

Many studies have been directed towards determining the influence that different parameters have on the level of volatile retention.

a. Solids Composition

The degree of volatile retention in freeze-dried liquid systems is strongly influenced by the nature of dissolved solids and, in some cases, by the presence of suspended solid material.

Saravocos and Moyer (1968) found that ethyl acetate, ethyl butyrate, methyl anthranilate and acetic acid in food gels were retained to different extents

depending on the material from which the gel is made. Low methoxy pectin retained less of the flavoring compound than pectin and cellulose exhibited a better retention capacity than gelatin or starch.

Flink and Karel (1970a, b) have determined the retention values of several volatile compounds with a variety of mono-, di- and polysaccharides which were freeze dried under identical conditions. The ability to retain volatiles decreased in the order; disaccharide, monosaccharide, polysaccharide. The retention of sodium chloride, a salt, was found to be less than one tenth that of the polysaccharide, dextran-10. Similar trends were noticed by Sugisawa et al. (1973) for the retention of n-propanol in freeze-dried solutions containing mono- and disaccharides.

Studies on the retention of 2-propanol in aqueous suspensions of cellulose and starch (Chirife and Karel, 1973a) revealed starch gave much higher retentions than cellulose even at identical initial solids content.

Chirife and Karel (1974b) demonstrated that the protein, pepsin, gave a significantly higher retention of 2-propanol than did bovine serum albumin even though both proteins were present initially at a 20wt% concentration.

Studies on binary systems at a fixed total solids concentration have yielded variable results (Ofcarcik and Burns, 1974). For some carbohydrate mixtures (lactose-glucose), the retention of pyruvic acid improved in a synergistic manner while in other mixtures no effects were noticed.

Massaldi and King (1974b) proved that the presence of colloidal matter (cloud) influenced the retention of d-limonene during the freeze drying of orange juice.

b. Dissolved Solids Content

In the first quantitative analysis of volatile retention during freeze drying, Rey and Bastien (1962) found that the retention of acetone was enhanced as successive amounts of glucose were added to an Earle-salt solution.

Saravocos and Moyer (1968) studied the retention of ethyl acetate, ethyl butyrate, methyl anthranilate and acetic acid in model food gels and found that the degree of volatile retention increased with the addition of glucose and sucrose prior to freeze drying.

In freeze drying slabs of malto-dextrin, the retention of methanol, propanol and n-pentanol was found

to approach 100% at initial malto-dextrin concentrations of 60wt%. At reduced malto-dextrin levels, the retention was much lower (Thijssen, 1972b).

Similar results were reported from volatile retention studies on orange juice (Sauvageot et al., 1969). An increase in the dry matter content resulted in increased retentions for myrcene, limonene and pinene. However, in the same experiments ethanol exhibited the opposite behavior.

A higher initial solids content has also been found to give substantially better retention of volatile flavor species in apple juice (Chandrasekaran and King, 1971). In this study ethyl acetate, n-hexanol and n-hexyl acetate were chosen as representative apple volatiles.

Flink and Karel (1970b) demonstrated that in model solutions containing glucose and acetone, acetone retention after freeze drying decreased as the initial glucose concentration decreased.

Chirife et al. (1973) have found similar results in the polyvinylpyrollidone-n-propanol system where PVP has been used as a water soluble polymer which partially simulates a protein in solution. At low solids concentration (below 10-20wt%), increases in the

solids concentration significantly elevated the degree of n-propanol retention.

Chirife and Karel (1973a) showed that increasing the amount of suspended starch and cellulose had a beneficial effect on the retention of 2-propanol, but the increase was much more pronounced with starch.

Chirife and Karel (1974b) noted similar behavior as protein concentrations were increased in aqueous solutions of pepsin and bovine serum albumin.

Using a mixture of four carbohydrate gums, up to a dissolved content of 3wt%, Kayaert et al. (1975) obtained a linear relationship between the retention of acetone and n-propanol and the initial gum concentration.

Rulkens and Thijssen (1972a) concluded, on the basis of retention experiments using methanol, n-propanol and n-pentanol in aqueous mixtures of malto-dextrin, that retention increases with increasing dissolved solids content up to a critical value above which no further increase in volatile retention could be obtained.

Sugisawa et al. (1973) have shown that n-propanol retention in glucose, maltose and sucrose solutions reaches a maximum at about 40 to 50wt% sugar. Increased retention with initial sugar concentrations above this value do not occur.

Ofcarcik and Burns (1974) reported that an increase in sucrose, glucose and lactose concentrations in model aqueous systems and Bermuda onion juice resulted in increased carbonyl (expressed as pyruvic acid) retention. A leveling off of carbonyl retention occurred at approximately 5wt% carbohydrate.

Natural volatile components in mushroom extracts were retained to a very high degree even at relatively low initial solids content (Bartholomai et al., 1975).

This observed increase in volatile retention as the dissolved solids content of the solution increases, forms the basis for preconcentrating liquid foods prior to freeze drying. Thijssen (1970) discusses the different processes available for concentrating liquid foods containing volatile flavoring compounds.

c. Initial Volatile Concentration

Most reports describing studies on the effect of initial volatile concentration on retention come from Flink and/or Karel and co-workers (Flink and Karel, 1970b, Kayaert et al., 1975, Chirife et al., 1973, Chirife and Karel, 1973a and Chirife and Karel, 1974b). All of these studies have indicated that an increase in

the initial volatile concentration, at constant dissolved solids, results in a decrease in the percentage of volatile retained.

Such findings are supported by the work of Bartholomai et al. (1975) who monitored benzaldehyde retention as a function of its initial concentration.

The results of Berry and Froscher (1969) appear somewhat inconclusive since there was no evidence of any relationship between initial volatile content and percent retention in freeze-dried orange juice.

Voilley et al. (1973), however, observed the opposite behavior. When they increased the n-alcohol concentration in a synthetic solution composed of sugars (glucose, sucrose and fructose), citric acid, calcium chloride, pectins and albumins, the percent retention increased.

Massaldi and King (1974a) showed that initial volatile concentration in freeze-dried liquid systems was very important especially when the initial volatile content exceeded the solubility limit of the volatile in the aqueous solution. In the region of the solubility limit a sharp drop in retention was noted and beyond the solubility limit an asymptotic level of retention was observed.

d. Heat Treatment of the Drying Sample

An increase in the ice front temperature and an increase in the heating plate temperature will cause respective improvements in mass transfer and heat transfer within the drying sample. Better heat and mass transfer on the drying sample obviously will increase drying rate. By calculation Thijssen (1972a) has predicted that higher volatile retention should result from more rapid drying. Rulkens and Thijssen (1972a) proved this experimentally by maintaining the ice front at a constant temperature while heating through the frozen layer and controlling the rate of drying by manipulation of the chamber pressure. As an example, drying at chamber pressures giving a doubling of the drying rate at an ice front temperature of -20°C resulted in an increase in 1-propanol retention from 65% (slow drying) to 85% (rapid drying). It should be noted that maintaining the ice front temperature at -20°C by heating through the dry layer gave similar volatile retentions as heating through the frozen layer, when the samples were dried at equal rates. Both Thijssen (1972a) and Voilley et al. (1973) have shown that as the ice front temperature decreases, volatile retention increases. In addition decreasing

the chamber pressure results in lower ice front temperatures. In the absence of collapse volatile losses with higher ice front temperatures have been attributed to a decrease of the solids matrix concentration as some of the ice crystals melt. The temperature of the ice front is also influenced, to some extent, by the rate at which the sample was frozen. It has been shown previously that pore size will increase with a decreasing freezing rate. An increase in pore diameter reduces the vapor pressure drop over the dry porous matrix and thus reduces the ice front temperature at a constant platen temperature and chamber pressure; thus causing an increase in volatile retention.

Collapse during freeze drying as discussed previously, is a phenomenon in which the matrix undergoes structural degradation due to the onset of viscous flow. If temperature conditions in the drying matrix are such that collapse occurs, substantial amounts of volatile are lost as has been verified by Bellows and King (1973) and Swinnen et al. (1976).

e. Freezing Rate

The rate at which a volatile containing liquid solution freezes has been shown to have a pronounced

effect on the level of volatile retention. It has been shown that the constitution of the frozen product is directly related to the rate of freezing. Ettrup Petersen et al. (1973) have systematically investigated seven freezing treatments on coffee extract and found that slower freezing treatments generally produce a higher level of volatile retention than a fast freezing treatment. However, samples of uniform thickness which were dried very slowly had less retention than samples dried slowly. Flink and Labuzza (1972) have shown that volatile retention in maltose solutions was 8 to 10 times greater in slowly frozen samples than in quickly frozen samples, whereas the freezing rate was not found to be as critical in dextrin solution. n-Propanol retention in quickly frozen samples of polyvinylpyrrolidone was similarly shown to be less than in slowly frozen samples when all other freeze-drying parameters remained invariant (Chirife and Karel, 1973b). This trend was also found by Massaldi and King (1974a) with sucrose solutions.

f. Sample Dimensions

Chirife et al. (1973) have shown that as the thickness of the freeze dried sample increased, the

degree of volatile retention decreased. Thijssen (1972c) reported similar results for volatile retention in layers of granules. Rulkens and Thijssen (1972a) have shown that for any layer thickness there exists an optimal granule size at which volatile retention is maximum. Ettrup Petersen et al. (1973) showed that in freeze-dried coffee granules, thicker drying samples exhibited higher retentions than thinner samples. These authors postulated that the thicker samples would freeze more slowly than thin ones, and result in a higher level of volatile retention as would be expected with a decreased freezing rate. Flink and Karel (1970b) observed that varying the surface area, while maintaining a constant sample thickness, had no effect on volatile retention.

Very high retentions can be obtained during freeze drying if the following conditions are satisfied; (i) high initial dissolved solids content; (ii) low freezing rate; (iii) low ice front temperature; (iv) high drying rate; (v) low initial volatile concentration; (vi) thin layer of sample. The preceding list should be considered as a generalization since in many cases, results contrary to those expected have been reported.

3.2.3 Mechanisms of Retention

Several theories have been advanced to explain why the various process parameters influence volatile retention during freeze drying.

a. Microregion Theory

Flink and Karel (1970a, b) have adopted the microregion theory to explain the retention of volatiles during freeze drying of liquid systems. The microregion theory is based on the fact that as ice crystals grow in the freezing sample, volatiles and dissolved solutes are excluded from the pure ice. During freezing, solute molecules will interact with each other by hydrogen bonding, thus producing a structure which will act as a cage to entrap homogeneously dissolved volatiles which are present in an immiscible phase. As water is removed during drying, interaction between solute molecules increases since the extent of water-solute interactions will decrease. Below a certain moisture content the degree of association between solute molecules will be very high and literally prevent movement of the trapped volatile.

Karel and co-workers have devised numerous

experiments to give support to the microregion theory. Flink and Karel (1970a) have shown by layering experiments that volatile retention principly occurs only in the layer which contained the volatile initially. Furthermore the volatile was homogeneously retained throughout the whole sample when the volatile was initially homogeneous within the sample. Volatile loss during rehumidification experiments was attributed to the degree of disruption of hydrogen bonds in the amorphous freeze-dried cake (Flink and Karel, 1972 and Chirife and Karel, 1974a). Rehumidification thus leads to the partial destruction of the cage structure which traps the volatile. Total destruction of the microregion comes only with total dissolution of the freeze-dried cake. Flink and Karel (1972) and Chirife and Karel (1974a) demonstrated that thermal energy also disrupted the structure of the microregion as evidenced by volatile loss at elevated temperatures.

Retention of volatiles and subsequent microregion disruption studies have been carried out with numerous systems; polyvinylpyrrolidone (Chirife et al., 1973), cellulose and starch suspensions (Chirife and Karel, 1974b), maltose (Chirife and Karel, 1974b) and mushroom extracts (Bartholomai et al., 1975). In all

systems the results were considered compatible with the microregion theory. In addition the investigators were able to correlate the retention influence of the various process parameters with the microregion theory.

3.2.3.2 Adsorption

Adsorption of volatiles on the dried matrix, as the volatile passes through the capillaries of the dry layer, has been considered to account for the high degree of volatile retention during freeze drying. Rey and Bastien (1962) attributed the high degree of acetone retention in glucose-containing systems to the adsorption of acetone onto glucose. Boskovic and Issenberg (1969) and Issenberg et al. (1968) have studied the adsorption and desorption of organic volatiles on food components.

Maier (1969, 1970, 1971, 1972) and Gray and Roberts (1970) studied the binding of various volatile organic compounds to food and food components and found strong interactions between specific substrates and some adsorbates. Lee et al. (1975) found that stable anhydrous α-lactose had a high capacity for adsorbing alcohols, esters and ketones.

Maier (1972) observed that sorption of ketones

usually required the presence of water to allow ketone penetration into polymeric aggregates or the presence of fat in which the ketones apparently dissolved. In the absence of water there was some sorption of acetone on zein, starch and pectin. The adsorption was irreversible. Infrared measurements confirmed that adsorption was due to (ketone) C=O---H-O (polymer) hydrogen bonding.

Chirife and Karel (1973b) showed that the adsorption phenomena could contribute significantly to the total amount of n-propanol retained in freeze-dried polyvinylpyrrolidone solutions. Hydrogen bond formation between the carbonyl moiety of the polyvinylpyrrolidone and the hydroxyl group of the alcohol was considered to be the main mode of interaction. Infrared studies by Strassmair et al. (1971) demonstrated that this type of hydrogen bond formation was plausible in the polyvinylpyrrolidone-n-propanol system. However it should be emphasized that Chirife and Karel (1973b) considered the amount of volatile retained by microregion entrapment far exceeded the amount retained by adsorption.

d. Diffusion Theory

When a liquid layer is cooled ice crystals grow perpendicularly to the cooled surface causing ice and solute fractions to be separated within the frozen product as depicted in Figure 17. As sublimation proceeds vacant spaces or pores remain. These pores separate the eutectic solids or CAS region. The volatiles are initially distributed throughout the solutes phase. As the sublimation front retreats from the sample surface, water within the CAS will diffuse into the vacant pores. The water content in the matrix, during this period of secondary drying will decrease with increasing distance from the ice front. Since the ice crystals are impermeable to volatiles, the volatiles can only escape from the matrix at or above the ice front by the process of diffusion.

Thijssen and Rulkens (1969) have presented a semi-quanitative diffusion analysis of volatile loss during freeze drying. This interpretation of volatile loss has been made using a binary analysis to calculate diffusion coefficients (Menting et al., 1970a) and to predict rates of loss during drying (Menting et al., 1970a, b). Earlier work by Menting and Hoogstad (1967a, b) showed that the movement of a volatile organic species

through a highly concentrated carbohydrate matrix is severely restricted. In fact at very low moisture contents, the carbohydrate matrix was considered to be impermeable to the flow of volatile but not to the flow of water. Explanations for this volatile impermeability come from the studies of Menting et al. (1970a) who showed that the diffusion coefficient of acetone in an aqueous malto-dextrin solution is substantially less than the diffusion coefficient of water in the same solution. On the basis of a binary diffusion model they proved that as the moisture content of the malto-dextrin solution decreased, the diffusion coefficients of volatile (acetone) and water decreased. Furthermore the decrease in the diffusion coefficient of volatile was much greater than the decrease in the diffusion coefficient of water. In coffee extract at approximately 95% dissolved solids, the ratio $D_{acetone}$ to D_{water} was close to 10^{-4} (Thijssen, 1972b). This illustrates that at very low water concentrations, as would prevail in the CAS, the system can be considered as being permeable to water only. The selective diffusivity is also strongly dependent on temperature. Temperature studies, again by Thijssen (1972b), have shown for example that at 25°C

for a ratio of Dacetone:Dwater of 0.01 the water content in a malto-dextrin solution would have to be approximately 10wt%, whereas at -30°C the water content would have to be 40wt% to give a similar Dacetone:Dwater value. This difference in diffusivity of volatile (as typified so far by acetone) and water forms the basis for the selective diffusion theory explaining volatile retention during freeze drying.

Chandrasekaran and King (1972b) and King and Chandrasekaran (1973) have extended the analysis of volatile loss during drying to a three component diffusion model as opposed to Thijssen's binary model. In the ternary model, the authors employed multi-component diffusion coefficients which they had previously measured in aqueous systems of volatile and sugar (Chandrasekaran and King, 1972a). Flux equations for volatile and water during drying were solved and suggested that, because of the sugar-water composition gradient formed during drying, the transport of volatile components would create a local accumulation of volatile species. This predicted local accumulation of volatile was verified experimentally by the sectioning of samples. Although the authors conceded that the previous binary diffusion analysis was useful

in a qualitative manner, the ternary diffusion model gave a much better quantitative explanation of observed volatile loss and concentration profiles. In addition the ternary analysis provided a better explanation for the effect of various processing conditions on volatile loss.

King (1970) has shown that the influence which different processing parameters may have on volatile loss can be qualitatively related to increasing or decreasing values of the Fourier group, Dt/L^2, as applied to individual regions within the CAS.

C. EXPERIMENTAL

1) Chemicals

Dissolved solids or substrates were sucrose (Baker), d-glucose (Fisher), sodium chloride (MCB) and gum arabic (Sigma) and were used without further purification. Carvone (K and K), piperitone (ICN), pulegone (Fluka), eugenol (ICN) and m-anisaldehyde (ICN) were found to be at least 90% pure by gas chromatographic analysis and were used without further purification. Ethanol (Canlab) and octanol (Baker) were used as received. Buffering salts were obtained from

Fisher. Potassium chromate (Fisher) lithium chloride (Fisher) and sodium dichromate (Baker) were used to prepare relative humidity chambers. Distilled water was used to prepare all solutions.

2) Equipment

A Model 42, RePP Sublimator (The VirTis Co., Inc.) was used to freeze dry the samples. This sublimator was equipt with a Hyvac 45 vacuum pump with a capacity of 15 ft^3/min and an ultimate dry chamber vacuum of 5 microns. Condenser and tray temperatures could not be independently regulated since the cooling of one automatically eliminated cooling of the other. Pressure measurements were made with a McLeod guage.

Ultraviolet absorption measurements were conducted on a Unicam SP1800 Ultraviolet Spectrophotometer which was equipt with a deuterium lamp for ultraviolet analysis. The instrument was operated on the fixed wave length mode using a band width of 1.2 mm and a slit width of 0.4 mm. Quartz cells (Canlab) were used for both reference and sample.

pH measurements were carried out with a Fisher Model 230 pH/ion Meter (Fisher). Certified buffer solutions (Fisher) were used to calibrate the pH meter.

A Virtronics temperature recorder (The VirTis Co., Inc.), in conjunction with a thermistor was used to monitor sample temperatures during freeze drying.

All glassware was Pyrex and was cleaned either with an alcoholic potassium hydroxide solution or a chromic acid solution. Prior to use all glassware was rinsed thoroughly with distilled water.

3) Sample Preparation

Aqueous solutions of the substrate were prepared on a weight percent basis. Volatile concentrations are expressed on a volumetric basis (ppm). Volatile containing solutions were prepared by one of two possible ways. Individual samples were prepared by injecting the desired volume of volatile, using a 10 µl Hamilton syringe, into a known volume of solution in a 50 ml Erlenmeyer flask. After the volatile was added to the matrix containing solution, it was necessary to vigourously shake the Erlenmeyer flask for at least several minutes to effect solubilization of the volatile as indicated by absence of an organic phase. Such a mixing procedure was required even for volatiles well below their solubility limit in the solution. Numerous analyses have shown that this technique of volatile

addition is reproducible to ±1.5%. When volatile-containing solutions were made in this manner, four samples were prepared, three for freeze drying and one as a reference which was stored at 4°C. Bulk samples containing volatiles were prepared by introducing weighed quantities of volatile into volumetric flasks and filling to the mark with the appropriate solution. The volumetric concentrations were then calculated using density data for the volatile.

When necessary solutions were stored in stoppered flasks at 4°C. To avoid possible interactions between the volatile and the stopper, the stoppers were enclosed in aluminum foil. All bulk solutions were prepared on a regular basis to minimize possible effects of microbial growth.

4) Freeze Drying

Prior to freezing, the samples (normally 5.0 ml) were weighed. The samples were frozen on the shelf of the freeze-drying apparatus. Before placing the samples in the freeze-drying apparatus, the shelf temperature was lowered to -40°C. When the shelf temperature had reached -40°C, the samples were quickly placed on the shelf and allowed to freeze. Since each

sample was prepared in triplicate each member of the triplicate was placed on a different shelf within the freeze drier. The sample temperatures were monitored by a reference sample containing the thermistor. This reference sample was the last sample to be placed in the freeze drier. When the reference temperature had reached -35°C (after approximately 1 h) the shelf cooling was switched off and the condenser cooling was switched on. At a condenser temperature of -40°C, the drying chamber was sealed and the vacuum pump was activated. The condenser temperature for all runs was -70°C. The samples were allowed to dry for 48 h without the input of any heat. After drying the samples were removed from the shelves of the freeze-drying apparatus and stoppered immediately.

5) Volatile Analysis

Immediately after freeze drying, the samples were weighed and rehydrated to their original weight. Volatile content was determined spectrophotometrically. Using pipets and volumetric flasks, the rehydrated samples were diluted with water such that the resulting volatile concentration gave an absorbance detectable by the ultraviolet spectrophotometer. The fourth member or

reference, which was kept stoppered at 4°C, was diluted in exactly the same fashion. The percent retention was calculated as a ratio of the absorbance of the rehydrated freeze-dried samples to the absorbance of the reference. Standard deviations were calculated on the basis of triplicate measurements. It should be noted here that the reference absorbance used in calculating the percent retention was not the absorbance of a single reference but generally the average of five or six reference samples.

In cases where samples contained volatile in excess of its solubility, both the freeze-dried samples and the reference sample were diluted to such an extent that all the volatile was homogeneously dissolved and then the dilutions for spectrophotometric analysis were performed.

All experiments were carried out with a view to minimize all variables during the study of a certain parameter during freeze drying. Data relating to any particular parameter was obtained from a single freeze-drying experiment and thus the comparison of results from different freeze-drying runs was avoided.

D. RESULTS

1) General Observations

The samples were dried for a period of 48 h. A temperature profile during freezing and drying over the 48 h period is shown in Figure 21. After drying the final sample temperature in all cases was between -3 and -5°C. Experiments conducted with no samples in the freeze drier showed that shelf temperatures decreased to -3 to -5°C due to the cooling effect of the condensers (-70°C) which are in close proximity to the shelves. Upon evacuation the chamber pressure decreased to between 20 and 50 microns after 15 min and at the end of all freeze-drying runs, the chamber pressure was invariably close to 10 microns.

In freeze-dried solutions of 10% sucrose, 10% glucose, 1% gum arabic and 5% sodium chloride it was found that the residual moisture content was approximately 1 to 2% after 20 h. By expressing the fractional water retention as a function of drying time, it is possible to obtain an estimate of the drying rate of each solution. Table 5 illustrates the calculated drying rates for the solutions as expressed in the relation,

$$y = mx + b$$

where y=% moisture remaining (wet basis) after a certain time represented by x. Values of m denote the drying rate (% water lost per hour on a wet basis) up to drying times of 12 h. Inspection of m values, tabulated in Table 5, illustrate that the drying rates of the four types of solutions employed are quite similar being between 5 and 6%/h.

All solutions appeared to freeze dry well as there was no evidence of structural collapse. Upon rehydration the samples appeared to "melt" as the cake structure disintegrated with the addition of water. With the exception of freeze-dried glucose samples, the cakes retained their structural integrity for several hours when exposed to the atmosphere. Freeze-dried glucose samples, however, immediately took on a semi-liquid appearance.

2) Volatile Retention

a. Drying Time

Retention of carvone as a function of drying time has been studied in 10% sucrose, 10% glucose, 5% sodium chloride and 1% gum arabic. Carvone, initially

at 500 ppm, was lost at a greater rate during the first part of the drying period when the water content of the sample was appreciable. At very low moisture contents (1 to 2%) carvone loss ceased and the percent retention remained constant even for extended periods of time under a vacuum of 10 microns. As a typical example, carvone retention as a function of drying time in 1% gum arabic is shown in Figure 22. In this Figure the vertical bars represent the standard deviation calculated on the basis of triplicates. Figure 22 also includes the moisture retention as a function of drying time. The retention of carvone in the other solutions was quite similar, differing only in the degree of retention after 48 h.

b. Sample Dimensions

Experiments were carried out to investigate the effect of sample geometry on carvone retention in 10% sucrose and 1% gum arabic solutions. Layer thickness studies were performed in beakers ranging in size from 10 to 125 ml. The layer thickness of the sample was varied by adding 5.0 ml of solution to each beaker, thus keeping the volume of sample constant for all thicknesses. Figure 23 illustrates that at a constant

initial volume of sample, carvone (500 ppm) retention increases as the layer thickness increases and the retention appears to level off at a layer thickness of approximately 8 mm.

Figure 24 shows that surface area of the freeze-drying sample has very little influence on the retention of carvone (500 ppm) in either 10% sucrose or 1% gum arabic. In these experiments the sample thickness was kept constant at 7 mm.

c. Dissolved Solids Content

Figures 25, 26 and 27 illustrate the beneficial effect that increasing initial sucrose content has on the respective retention of carvone (500 ppm), m-anisaldehyde (500 ppm) and eugenol (500 ppm). Previous solubility studies have shown that at 500 ppm concentrations all of the volatiles are well below their solubility limit in the sucrose solutions. In each case the volatile retention increases in a linear fashion with increasing initial sucrose content. In addition at initial sucrose contents of between 20% and 25% the retention of the volatiles appears to level off. Freeze drying of sucrose solutions at initial concentrations of 30% or greater was unsuccessful since

the samples appeared to melt while drying. Because the shelf cooling of the freeze-drying apparatus could not be operated independently of the condenser cooling, this problem of melting could not be overcome.

Figure 28 reveals an increase in volatile retention with increasing gum arabic content. In each case the volatile retention increases linearly with increasing initial gum arabic. Figure 28 shows that the retentions of carvone and m-anisaldehyde are very similar at the same initial gum arabic concentrations. However, Figure 28 also illustrates that at a given initial gum arabic content the retention of eugenol is at least 20% greater than the retention of carvone or m-anisaldehyde. The degree of retention of eugenol in gum arabic appears to level out at an initial concentration of 4%.

Data on the retention of carvone, m-anisaldehyde and eugenol in glucose solutions, are presented in Table 6. In each case the volatile was present initially at 500 ppm. Inspection of Table 6 points out several interesting features. As the initial glucose content increases from 3 to 7wt%, the volatile retention increases substantially. Above 7% initial glucose the retention of the volatiles appears to stabilize. This is in

sharp contrast to the sucrose case where stabilization of retention values occurred at approximately 25%. Although the glucose solutions, ranging from 3 to 15%, appeared to freeze dry well, the standard deviations tabulated in Table 6 often approach 10% of the mean value determined from the three samples. Solutions containing glucose initially above 15% could not be freeze dried successfully under the experimental conditions used because melting of the sample occurred.

Table 7 illustrates that an increased initial sodium chloride content causes an increase in the retention levels of carvone and m-anisaldehyde. The percent retention for both of these volatiles is seen to be much lower in sodium chloride solutions than in sucrose, glucose or gum arabic solutions. Data for the retention of eugenol in sodium chloride were not obtained because the absorbances of the rehydrated sodium chloride solutions were greater than the absorbances of the reference samples.

d. Nature of the Volatile Species

Inspection of Figures 25, 26 and 27 indicate that the respective retentions of carvone, m-anisaldehyde and eugenol in sucrose solutions are very similar. Each volatile has a retention level of 30 to 40% at 5% sucrose and the retention increases in a fairly linear manner to approximately 90% at 25% sucrose in all cases. Carvone and m-anisaldehyde have similar retentions in all gum arabic solutions as evidenced in Figure 28, however, the eugenol retention in the gum arabic solutions is significantly higher than carvone or m-anisaldehyde. Table 6 shows that m-anisaldehyde and eugenol appear to have a slightly higher retention level than carvone in glucose solutions. Carvone retention in sodium chloride solutions is substantially below that of m-anisaldehyde as evidenced in Table 7.

The terpenic essential oil components, carvone, pulegone and piperitone, all have the same basic hydrocarbon skeleton and differ only in the position of the carbonyl group and/or the position of the double bond. Due to their similar structures and very similar molecular weights, retention experiments were conducted in 10% sucrose, 10% glucose, 5% sodium chloride and 1% gum arabic. At an initial volatile

concentration of 500 ppm, the three volatiles were retained to very similar extents as evidenced in Figure 29. Piperitone in 10% sucrose exhibits a 10% higher retention than carvone or pulegone.

e. Initial Volatile Concentration

Figures 30 through 34 illustrate the respective retention of carvone, pulegone, eugenol, piperitone and m-anisaldehyde as a function of initial volatile concentration in a 10% sucrose solution. In these figures percent retention is plotted against the parameter, n, which represents the ratio of initial volatile concentration to the volatile solubility in 10% sucrose as measured at 10°C. For all volatiles n ranged from approximately 0.2 to 1.4. Figures 30 through 34 invariably show that volatile retention decreases with increasing values of n. For values of $n<1$, the volatile retentions appear to decrease in a regular fashion. Carvone and pulegone, the least soluble of the volatiles, exhibit a sharp decrease in retention at n values close to 1 and the retention level appears to level out when $n>1$ (Figures 30 and 31). A similar trend is revealed in Figure 32 which illustrates eugenol retention as a function of n. However,

it can be seen that the dip in the curve at n values close to 1 is not as pronounced as in the carvone and pulegone cases. For n>1, the eugenol retention appears to stabilize. m-Anisaldehyde and piperitone, the most soluble of the volatiles, do not exhibit this pronounced decrease in retention at n values near 1 as evidenced in Figures 33 and 34. The respective solubilities of m-anisaldehyde and piperitone in 10% sucrose at 10°C are 2690 and 2820 ppm. A definite inflection point is observed for m-anisaldehyde at n near 1 as, once again, the retention level appears to stabilize for n>1 (Figure 33). Figure 34 illustrates that the curve relating piperitone retention to n decreases in a regular fashion with no inflection points discernable.

Figures 35, 36 and 37 depict the respective retentions of carvone, pulegone and piperitone as a function of n in 1% gum arabic solutions. In all cases a steady decrease of volatile retention is observed as n is increased to values greater than 1.

f. Freezing Rate

Table 8 illustrates the retention of carvone and piperitone in various solutions as a function of the sample freezing rate. Fast freezing was accom-

plished by immersing the samples in liquid nitrogen for a period of 3 min prior to loading on the shelf of the freeze dryer at -40°C. Slow freezing was performed by placing the samples on the shelf of the freeze dryer which was previously cooled to -40°C. In all samples, with the exception of sodium chloride, it is apparent that the fast freezing treatment gave higher retentions of carvone and piperitone during freeze drying.

g. Influence of Added Volatile

The retentions of carvone, eugenol and m-anisaldehyde in 10% sucrose was studied when another volatile compound was present in the freeze-dried solution. Ethanol was used as an infinitely water soluble volatile. Table 9 shows that the retentions of carvone, eugenol and m-anisaldehyde are independent of the initial ethanol concentrations within the range studied. Octanol was chosen as a relatively insoluble volatile (approximately 590 ppm in water). It is evidenced that increasing the initial octanol concentration has the overall effect of reducing the retention level of carvone, eugenol and m-anisaldehyde in 10% sucrose as shown in Table 10. More specifically

carvone and eugenol retentions decrease in a steady manner, whereas the m-anisaldehyde results appear somewhat erratic, although the trend to decreasing retentions with increasing octanol is evident.

h. pH of Freeze-Dried Solutions

Retention values of carvone and eugenol in 10% sucrose as a function of initial solution pH are depicted in Figure 38. The pH values of Figure 38 are those of the aqueous sample containing sucrose and volatile i.e. the pH of the solution immediately before freeze drying. It is evident that both carvone and eugenol retention values reach a minimum near neutrality and attain very high values at the upper and lower ends of the pH scale. As evidenced in Figure 39 both piperitone and pulegone retentions exhibit exactly the same behavior, with a varying pH in 10% sucrose. In these experiments water was treated with hydrochloric acid or sodium hydroxide to produce aqueous solutions from which the 10% sucrose solution was prepared. The volatile was then added to give volatile concentrations of 500 ppm. The pH values of the solutions at various stages of preparation and after freeze drying are given in Table 11. It is evident

that the pH values at various stages are generally quite constant although in some cases variation is observed. The greatest variation is seen to occur in the highest pH values of the rehydrated freeze-dried samples. For each of the four volatiles, the highest pH value decreases approximately 1.5 pH unit from the pH values measured at previous stages of the experiment.

The results of pH influence on carvone retention in 5% sodium chloride are tabulated in Table 12. pH appears to have only a slight influence on the degree of retention of the volatile.

Carvone (500 ppm) retention in 10% glucose as a function of pH is shown in Figure 40, O. Once again carvone retention is lowest near pH 7 with increasing levels of retention at higher and lower pH values. Figure 40 also illustrates eugenol (500 ppm) retention, in 10% glucose with varying pH. The retention of eugenol increases on the basic side of neutrality, however at the low pH value of 2.7, the retention is slightly lower than observed retentions in the neutral pH range. The pH values at various stages of the experiment were similar but, as was the case with sucrose, a significant decrease was observed for the highest pH value of the rehydrated

freeze-dried solution.

Figure 41 illustrates the retention of carvone and eugenol as a function of initial pH in 1% gum arabic solution. It can be noted that each of these volatiles exhibits a minimum retention at pH values close to 5. Figures 42 and 43 illustrate similar trends for piperitone and pulegone respectively in 1% gum arabic solutions. The retentions in solutions where the pH has been adjusted by hydrochloric acid or sodium hydroxide are denoted by the symbol, O. The pH values of the gum arabic solutions at different stages of the experiment are given in Table 13. Gum arabic was found to exhibit a strong buffering action since when added to water or water adjusted to pH 9 with sodium hydroxide, a resultant pH very close to 5 was invariably obtained. Acid solutions, initially at pH 3, became slightly more basic as the pH increased to approximately 4 when gum arabic was added. Highly basic solutions (pH 10 to 11) were less affected by the addition of gum arabic. The most basic pH values recorded after freeze drying decreased by 1 to 1.5 pH unit from observed values prior to freeze drying. This phenomenon was observed previously with sucrose and glucose.

Gum arabic solutions of pH 6.8 and 9.1 were

prepared by adding gum arabic to water buffered to these pH values. Buffering solutions were chosen to investigate volatile retention in 1% gum arabic in the pH range 5 to 9 because the addition of dilute sodium hydroxide, in an attempt to raise the pH above 5, would have altered the gum arabic concentration. The pH profile of the buffered solutions was found to be constant throughout all stages of solution preparation except a slight decrease of 0.2 pH unit was measured for the rehydrated samples initially at pH 9.1. Figures 42 and 43 include the respective retentions of piperitone and pulegone at pH values of 6.8 and 9.1 and are denoted by the symbol ▽. Thus it appears that volatile retention in gum arabic solutions increases steadily with increasing pH for pH values greater than 5.

i. Layering Experiments

To investigate the possibility that adsorption might play a role in the retention of volatiles, the distribution of the retained volatiles in 10% sucrose and 1% gum arabic was studied using carvone as a representative volatile. These experiments were conducted by freezing a layer of solution containing no volatile

on top of a previously frozen solution containing carvone (500 ppm). For 10% sucrose a percentage retention level of 58.1±0.6 was observed when the layering was performed with no mechanical separation between the two layers. When the layers were separated by placing a screen between the two layers and the upper and lower layers were analyzed individually, a total retention (sum of retention in upper (3.3±0.5) and lower (53.6±0.3) layer) of approximately 57% was obtained. Thus it appears that approximately 5% of the volatile is retained in the upper layer.

Similar experiments with gum arabic revealed an overall increase in retention as a non-volatile containing 1% gum arabic solution was layered on a frozen gum arabic solution containing carvone. Analyses of the upper and lower layers after freeze drying yielded a total percentage retention of 32.7±0.6 (sum of retention in upper (4.5±0.2) and lower (28.2±0.7). The percent retained in a single carvone containing layer was found to be 26.8±2.7.

j. Rehumidification

Freeze-dried samples of 10% sucrose containing carvone were exposed to atmospheres of different

relative humidity (Wink and Sears, 1950) for extended periods of time. The carvone content was monitored at various times up to 80 h. Figure 44 illustrates carvone retention (expressed as the ratio of carvone content after a certain time to the initial carvone content) as a function of time for each of the three relative humidities. It is evident that the final carvone content is strongly dependent on the relative humidity. The freeze-dried sucrose cakes retained their structure at 11.1% relative humidity after 80 h and were very easily and quickly rehydrated. At relative humidities of 50.8 and 86.5% the cakes showed obvious signs of disintegration and these samples were not quickly rehydrated.

k. Extension of Volatile Retention Studies to Systems of Lower Volatile Concentration

To investigate the possibility of using the ultraviolet spectrophotometric method of analysis to monitor very low volatile concentrations (i.e. less than 500 ppm as was most generally used), 10% sucrose solutions containing carvone and piperitone at 10, 25 and 50 ppm were freeze dried and analyzed for volatile. Although no retentions were calculated, the absorbances

of the rehydrated freeze-dried samples, as tabulated in Table 14, are substantial and could be used in determining retention values at such reduced volatile concentrations.

It was found that when analyzing solutions containing sucrose in relatively large amounts (10%), the sucrose solution had to be used in the reference cell of the ultraviolet spectrophotometer. In such cases the use of water as a reference was found to cause errors of 7 to 10% in the absorbance reading of the volatile.

E. DISCUSSION

The high degree of volatile retention during the freeze drying of aqueous solutions has been attributed to adsorption, microregion formation or selective diffusion. At the present time adsorption is considered to play only a minor role in contributing to the overall retention of volatile flavoring compounds during freeze drying. The work of Chirife and Karel (1973b) has shown that only a small portion of the retained volatile may be accounted for by adsorption while the bulk of the volatile is retained by some other mechanism. Layering experiments with the essential

oil component carvone as used in this study also indicates that only a small fraction of the volatile retained may be attributed to adsorption.

Microregion entrapment, as favored by Karel and Flink and co-workers, or selective diffusion, as supported by King and Thijssen and co-workers, are considered to be the only plausible mechanisms which explain volatile retention at the present time. Both the microregion theory and the selective diffusion theory have been successfully applied to freeze-dried systems. In the opinion of several authors (King and Massaldi, 1974 and Flink, 1975b), these two proposed mechanisms describe the same phenomena from two different approaches, namely mathematical or macroscopic vs. morphological or microscopic viewpoints.

Figures 25, 26 and 27 show that the respective retentions of the essential oil components carvone, m-anisaldehyde and eugenol significantly increase as the initial content of the dissolved sucrose increases. In addition these Figures show that the volatile retention appears to level out at an initial sucrose content of between 20 and 25%. Bellows and King (1973) have investigated the collapse phenomena associated with freeze-drying sucrose solutions. The authors reported

that the collapse temperatures of sucrose samples varied slightly with initial sucrose content, with a 25% sucrose sample having a collapse temperature of -24°C. As noted in the Experimental section, the samples were cooled to -35°C, a temperature well below the sucrose collapse temperature. As shown in Figure 21, the sample temperatures remained well below the collapse temperature for a considerable length of time during drying. Thus it was concluded that the sucrose solutions freeze dried well i.e. without collapse. Additional proof that the sucrose solutions freeze dried without collapse was found in the ability of the freeze-dried product to be quickly and completely rehydrated.

Bellows and King (1973) and Ito (1970a) showed that the collapse temperature of a freeze-drying sample increased as the average molecular weight of the dissolved solids increased. This fact in conjunction with the excellent rehydration characteristics of the freeze-dried gum arabic solutions suggested that the gum arabic solutions freeze dried well. As indicated in Figure 28 gum arabic possess an enormous ability to retain volatile during freeze drying. Comparison of Figure 28 with Figures 25, 26 or 27 shows that a 1% gum arabic solution retains a significantly greater

proportion of volatile than a 5% sucrose solution. The ability of gum arabic to "lock in" or "encapsulate" flavoring compounds is very well known and has been used to great advantage in spray-drying operations (Glicksman, 1969). Kayaert et al. (1975) showed that a mixture of four carbohydrate gums gave very high retentions of acetone and n-propanol at low initial gum concentrations of 3%. Thus it appears that the gums, in contrast to other macromolecular species, give a higher volatile retention than the simpler sugars. Chirife and Karel (1973a) have shown that the degree of volatile retention in solutions containing a macromolecular species (starch, cellulose and dextran 10) is generally much lower than for solutions containing either a mono or disaccharide. Thus ability of gum arabic to retain volatiles to such a high degree is likely due to its ability to form a crosslinked network. Thus the viscosity of the CAS regions in frozen gum arabic solutions would be greater than the viscosity of sucrose CAS regions at the same temperature. Since the diffusion coefficient of the volatile within the CAS is dependent upon the viscosity of the CAS, it follows that volatile retention in the gum arabic solutions will be greater than retention values in sucrose solutions.

As evidenced in Table 6, increased initial glucose results in increased volatile retention. However, the observed increase in volatile retention in the glucose samples appears less regular than that found previously with sucrose or gum arabic. Table 6 also illustrated that the calculated standard deviations often approach 10% of the mean retention value. Bellows and King (1973) and Ito (1970a) found that the collapse temperatures of freeze-drying glucose solutions were very close to -40°C. Thus it is probably true that the glucose solutions, especially the more concentrated samples, collapsed during freeze drying. Bellows and King (1973) and Swinnen et al. (1976) have shown that volatile retention decreases with the onset of collapse during freeze drying. The data for carvone and m-anisaldehyde presented in Table 6 indicate that collapse occurred in the more concentrated glucose solution (10 and 15%) since the retention values should be significantly higher as would be the case if collapse had not occurred.

On the basis of the results of Ito (1970a) it was assumed that the sodium chloride solutions freeze dried well. Ito (1970a) found that sodium chloride solutions undergo collapse at -22°C, well above the temperatures used in this study. Table 7 illustrates

that dissolved salts as well as carbohydrates may retain carvone and eugenol to an appreciable extent. Retention values of eugenol in sodium chloride solutions were not obtained since it was suspected that sodium chloride and eugenol reacted chemically. The ultraviolet characteristics of sodium chloride and eugenol solutions were very different from those of eugenol in pure water.

The increase in volatile retention with increasing dissolved solids content may be a consequence of more hydrogen bonding (microregion theory) or reduced Dt/L^2 values for the volatile. However in the sodium chloride system, where significant volatile retentions are observed, the microregion entrapment mechanism would appear to be inoperative since sodium chloride can form no hydrogen bonds. Thus it appears that the selective diffusion theory would offer the most probable explanation for volatile retention in this case. However, it should be pointed out that the selective diffusivity of water at low moisture concentrations has been verified only on non-crystalline hydrophilic organic systems and not in an inorganic system such as one containing sodium chloride.

The retentions of pulegone and piperitone as influenced by the initial dissolved solids content were

not determined. Since carvone, pulegone and piperitone have similar molecular weights, the same carbon skelton and the same functional groups, it was expected that these three compounds would exhibit very similar retentions. Figure 29 does indeed show that these three terpenic compounds do have similar retentions in sucrose, glucose, sodium chloride and gum arabic solutions. On the basis of the selective diffusion theory, the degree of volatile retention may be qualitatively related to the value of the diffusion coefficient of the volatile within the CAS. Due to the similarities in molecular weight, structure and functional groups, the diffusion coefficients of carvone, pulegone and piperitone would be expected to be very similar. Figures 25 through 28 and Tables 6 and 7 generally show that volatile retention decreases in the order; eugenol > m-anisaldehyde > carvone. Because these three compounds vary in molecular weight, shape and chemical structure it is expected that they would exhibit different diffusion characteristics and consequently different levels of volatile retention. It is conceivable that within the CAS regions, the volatiles might interact with the dissolved solids. Eugenol, for example, contains a hydroxyl group which might enter into hydrogen bonding with one of the many hydroxyl groups present in

the dissolved solute. m-Anisaldehyde and carvone might similarly interact with the dissolved solid through their carbonyl groups.

Inspection of Figures 25, 26 and 27 reveals that when retention curves are extrapolated to 0% sucrose, the plot will not pass through the origin but rather intersects the ordinate at retention values greater than zero. Retention experiments with carvone dissolved in water showed, that in the absence of dissolved solids, the volatile retention was zero. Therefore it appears that the effect of dissolved solids is most pronounced at very low dissolved solids content (0 to 5%). Figures 25, 26 and 27 indicate that for carvone, m-anisaldehyde and eugenol respectively, the volatile retention due to the first 5% dissolved solids approaches 35%. No other portion of these retention curves exhibits such a marked influence on volatile retention over a range of 5% dissolved solids. A similar situation is found with freeze-dried gum arabic solutions as evidenced in Figure 28. In this case, with carvone as an example, the retention increases from zero without any dissolved solids to approximately 40% at 1% initial gum arabic concentration so once again the marked influence of initially

low dissolved solids is evident.

Figure 24 illustrates that at a constant layer thickness the degree of carvone retention is independent of the sample area in freeze-dried sucrose and gum arabic solutions. This result is compatable both with the microregion and selective diffusion theories in that the area of the sample would not be expected to influence the nature of the CAS regions formed during freezing. Being of equal thicknesses all samples would freeze at the same rate hence in all cases the thickness of pure ice regions and the thickness of the CAS regions would be similar. Flink and Karel (1970b) found similar results for glucose and dextran-10. Figure 23 illustrates carvone retention in 10% sucrose and 1% gum arabic as a function of sample thickness. In both cases the sample retention increases with sample thickness until a thickness of approximately 8 mm is reached. At greater thicknesses the carvone retention appears to become independent of the sample thickness. This trend of increasing volatile retention with increased sample thickness was also observed by Ettrup Petersen et al. (1973) in samples of freeze-dried coffee. These findings of increased volatile retention with increased sample thickness appear to conflict

with the results of several investigators (Flink and Karel, 1970b and Bartholomai et al., 1975) who have found that volatile retention increases as sample thickness decreases. An explanation for greater volatile retention in thin samples is based on the fact that in thin samples rapid drying and steep moisture gradients would decrease the time during which the moisture content would remain at levels high enough to permit volatile escape. However, as pointed out by Ettrup Petersen et al. (1973) most literature regarding the effect of sample thickness on volatile retention considers primarily the dehydration phase of freeze drying. The authors postulate that the higher volatile retentions found with thicker samples is due to the different freezing rates of the thin and thick samples. The thick samples freeze more slowly than the thin ones and hence exhibit a greater volatile retention. This explanation of increased volatile retention with increased sample thickness, as proposed by Ettrup Petersen et al. (1973), would appear to explain the results presented in Figure 23 in a satisfactory manner.

Retentions of carvone, pulegone, eugenol, m-anisaldehyde and piperitone as a function of initial volatile concentration are shown in Figures 29 to 34

respectively. The initial volatile content as recorded on the abscissa is represented by the ratio of initial volatile concentration (ppm) to the saturation concentration (ppm) of the volatile in 10% sucrose solutions. This ratio is symbolized by n. The respective solubilities of the above volatiles in 10% sucrose solution were found to be 1560, 1490, 2052, 2690 and 2820 ppm at 10°C. All volatiles appear to exhibit a steady decrease in retention as n approaches a value of 1. Figures 29 and 30 respectively illustrate that the carvone and pulegone retention curves exhibit a sharp dip to lower retention values at n values very near 1. Both carvone and pulegone were shown to have very similar solubilities in 10% sucrose solutions. The retention values of carvone and pulegone appear to level off for n>1. Of the compounds investigated, eugenol has an intermediate solubility of 2052 ppm in 10% sucrose. Figure 31 illustrates that the dip in the retention curve at near 1 is very much less pronounced than that of carvone or pulegone. Again when initial eugenol content exceeds the solubility limit (n>1), the eugenol retention appears to level off. The retention curve for m-anisaldehyde, as shown in Figure 33, exhibits no deflection whatsoever at the

solubility limit however the retention levels for m-anisaldehyde appear to become more constant when the solubility limit is exceeded. The retention of piperitone as a function of its initial concentration is shown in Figure 34. It is evident that piperitone retention decreases steadily with increasing values of n.

Massaldi and King (1974a) have studied the retention of d-limonene and n-hexyl acetate as a function of initial volatile concentration and obtained retention curves very similar to those illustrated in Figures 29 and 30. In addition these workers were able to calculate theoretical retention curves for 25% and 10% sucrose solutions which predicted experimental results quite well especially for n-hexyl acetate in 25% sucrose. In the calculation of the theoretical model, Massaldi and King (1974a) assumed that the retentions of volatile initially present below the saturation limit would be constant because these volatiles would be homogeneously dissolved. Figures 29 to 34 show that the retention in solutions where the volatile content is initially below saturation are not constant and decrease with increasing initial volatile content. This decrease in volatile retention at initial volatile contents below saturation may be attributed

to the solubility limit of the volatile being exceeded during the freezing process and thus giving rise to pure droplets of volatile. If these droplets are in close proximity to the vapor phase after sublimation of the ice they will be totally lost through evaporation when exposed to the vacuum. According to Massaldi and King (1974a) the droplets entrapped within the CAS and not in contact with the vapor phase will be largely retained as will that portion of the volatile which remains homogeneously dissolved within the CAS.

Although the retention studies of Massaldi and King (1974a) were directed more to emulsified systems rather than toward unsaturated systems ($n<1$) several favorable comparisons may be made with this work. In both studies volatile retention appears to become constant as the initial volatile content exceeds the solubility limit. It has been previously shown (Figures 20 to 34) that as the solubility of the volatile decreases, more pronounced inflections of the retention curve occur at n values near 1. Massaldi and King (1973) have shown that the solubilities of n-hexyl acetate and d-limonene are respectively 509 ppm and 13.8 ppm in water at 25°C. Thus it would be expected that more pronounced inflections would

occur in retention curves for these compounds than those obtained in this work. The curves presented by Massaldi and King (1974a) appear to verify this prediction to a certain extent.

Microscopic observations by Flink and Gejl-Hansen (1972) indicate that the solubility characteristics of volatile compounds are a very important factor in determining volatile retention during freeze drying. Photographs of freeze-dried malto-dextrin solutions revealed droplets of 1-butanol and diacetyl. On the basis of solubility data reported by Flink and Gejl-Hansen (1972), it is expected that droplets of 1-butanol and diacetyl were formed during the freezing of the malto-dextrin solutions since the initial volatile concentrations used by these workers suggest that the volatile containing solution was homogeneous prior to freeze drying. Droplets of the relatively insoluble volatile hexanal were also observed however the source of these droplets is somewhat uncertain. These authors report that the hexanal containing solutions prepared prior to freeze drying appeared homogeneous and further state that these highly insoluble compounds such as hexanal are present in the initial solution as small drops. If the droplets present in

the freeze-dried malto-dextrin originated from a homogeneous solution, their formation could be attributed to the solubility limit being exceeded during freezing. However if the initial solution was in fact a suspension then the droplets present in the freeze-dried malto-dextrin could be identified with the droplets originally present. Obviously a precise knowledge of the solubility characteristics of these slightly soluble compounds would be useful in clarifying this ambiguity. A knowledge of the solubility parameters of hexanol in malto-dextrin solutions would similarly facilitate an interpretation of the microscopic studies of Flink et al. (1973). However, retention and microscopic data presented by Flink and Gejl-Hansen (1972) do point out that the degree of retention of highly insoluble volatiles is much lower than that of very soluble compounds and therefore confirms the prediction of Massaldi and King (1974a) that droplets near the gas pores will be lost during the drying stage and droplets embedded within the carbohydrate matrix will be largely retained.

Many studies have shown that the degree of volatile retention during freeze drying is greatly affected by the rate at which the liquid sample is

frozen (Flink and Labuza, 1972 and Chirife and Karel, 1974b). It has generally been found that the degree of volatile retention is significantly reduced as the freezing rate of the sample increases. The data presented in Table 8 appear to contradict previous finding since in all cases, with the exception of sodium chloride, the retentions of carvone and piperitone increase with an increased freezing rate. The increased retention with greater freezing rates are most apparent in the sucrose and glucose solutions. Most previous studies directed toward the influence of freezing rate on volatile retention have been carried out using infinitely water soluble volatiles. Massaldi and King (1974a) have determined that the retention of emulsified d-limonene in 25% sucrose solutions decreases as the sample freezes more quickly. A possible explanation for the results of Table 8 is offered by Thijssen (1972c). During freezing, which is in fact a freeze concentration of dissolved solids and volatiles, the sparingly soluble volatiles become supersaturated and segregate in the form of dispersed droplets. This droplet formation has been observed by Flink and Gejl-Hansen (1972). Because these droplets will be preferentially formed at or near the ice crystals, the droplets will

come into direct contact with the open gas pores after the sublimation front is passed. As stated by Massaldi and King (1974a) these droplets will evaporate completely. Therefore if there are volatiles present which will become supersaturated during freezing, the size of the droplets and consequently the probability of an open contact with the ice crystals will increase with a decrease in freezing rate. For these systems a decrease in the freezing rate therefore will result in a lower volatile retention. The combined results of Flink and Gejl-Hansen (1972), Massaldi and King (1974a) and this work appear to lend support to the prediction of Thijssen (1972c).

Massaldi and King (1974a) have suggested that the presence of an immiscible liquid phase, in a product that is to be freeze dried, may adversely effect the retention of important flavoring volatiles. An immiscible phase would extract useful volatile components from the aqueous mixture and thus the useful volatiles would be more susceptible to loss during the drying stage. The results presented in Table 10 indicate that the presence of immiscible octanol does indeed cause a marked decrease in the retentions of carvone, eugenol and m-anisaldehyde. The solutions with initial octanol

concentrations of 600 ppm and 800 ppm were non-homogeneous since the solubility limit of octanol in the 10% sucrose solution was exceeded. It is apparent that increasing amounts of initial octanol above the solubility limit cause increased losses of volatile. It is also apparent that octanol, initially present at levels below the solubility limit, decreases the retention of the volatiles under consideration. In all probability this homogeneously dissolved octanol separates as pure liquid as the solution is cooled and then extracts the other volatiles in much the same manner as the initially immiscible octanol. Table 10 also suggests that the different volatiles (carvone, eugenol and m-anisaldehyde) are extracted to different extents by the octanol since the decrease in retention is not the same in all cases. King and Massaldi (1974) have discussed the implications of having an immiscible phase present in a liquid food that is to be freeze dried. Table 9 illustrates that the retentions of carvone, eugenol and m-anisaldehyde are not affected by the presence of varying amounts of ethanol which is an infinitely water soluble volatile.

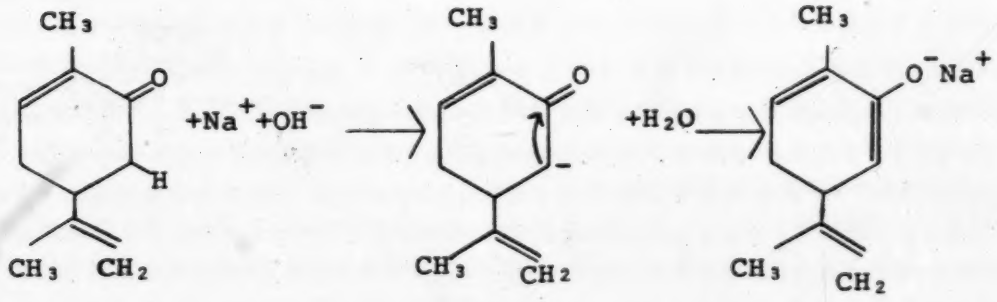
Figures 38 and 39 illustrate that retention of the essential oil components in 10% sucrose is very

dependent on the solution pH as measured prior to freeze drying. The four volatiles represented in Figures 38 and 39 all have very similar retention curves which exhibit a minimum at pH values close to neutrality and increase toward the extreme ends of the pH scale. Inspection of the literature shows that the effect of pH on volatile retention has not been previously studied to any great extent. Chalmers and Watts (1972) have investigated the effect of pH at the start of freeze drying on the recoveries of several organic acids of biological interest. These freeze-drying studies, which were conducted without any dissolved solids, indicated that the different acids were retained to different extents depending on the values of their heats of vaporization or sublimation. No general trends could be found relating retention with increasing pH values. Voilley et al. (1973) noted in their alcohol retention studies that the pH of the solution prior to freeze drying was 2.3. The complex model solutions employed by these investigators contained citric acid which would account for the low pH values measured.

The effect that pH has on retention, as revealed in Figures 38 and 39, could be related to several factors. In the first place it is possible that

the pH could alter the chemical nature of the volatile. Secondly it is possible that the pH may influence the characteristics of the dissolved solids. In addition the observed trends may be due to a combination of both of the above possibilities.

To check the first possibility the solubility of carvone in water and 10% sucrose was measured as a function of pH. The results of this study, conducted at room temperature, showed that the carvone solubility in water and 10% sucrose was constant in the pH range 2.7 to 11.0. These findings suggest that the chemical nature of the carvone molecule remains intact throughout the pH range studied. It was suggested (Fouron, 1977) that the carvone may react with base at high pH values according to the following reaction scheme.



If such a reaction were to take place the solubility of the carvone would be significantly increased because the reaction product would have the structure of a salt and therefore enhanced water solubility. Additional proof that the carvone remains intact at all pH values is found in the ultraviolet characteristics of the solutions. Carvone dissolved on water exhibited a maximum absorption at 241.5 mm. All solutions in which the pH was adjusted gave maximum absorptions at exactly the same wavelength. If the above reaction was to occur, the ultraviolet absorption properties of the salt would be entirely different from that of unreacted carvone because the ultraviolet absorption of carvone at 241.5 mm is due to electronic transitions involving the double bond within the six-membered ring and the carbonyl moiety. One could intuitively predict, on the basis of the results of Figures 38 and 39, that pH does not influence the nature of the volatile compound. It is unlikely that pH would affect eugenol (a non-terpenic essential oil component) and carvone, piperitone and pulegone (terpenic essential oil components) in exactly the same way since these compounds have very different chemical structures. Thus it appears that the influence pH has on retention

does not result from changes arising in the volatile.

It is well known that the sucrose molecule may break down in acidic or basic solution (Honig, 1953). In acidic solutions sucrose may be hydrolyzed to glucose and fructose. The rate of this hydrolysis reaction increases with a decrease in pH and increases with temperature. Stadler (1932) has correlated sucrose hydrolysis data over the range 50-120°C and 4.6-7.2 pH. Using Stadler's data a rough calculation has shown that at 20°C and pH 3.0 approximately 0.031% of the sucrose would be inverted in one hour. When sucrose solutions were prepared at low pH values, the solutions were immediately freeze dried and were not subjected to any high temperature. Thus it may be concluded that under the experimental conditions employed, sucrose hydrolysis would not take place and the sucrose molecules in solution retain their characteristic structure. Under alkaline conditions sucrose undergoes decomposition with the formation of furfural, methylglyoxol, acetone, lactic acid, trioxcglutaric acid, acetic acid, formic acid and several other acids which have not yet been characterized (Yudkin et al., 1971). This decomposition is accompanied by the formation of unknown mixtures of substances in very small quantities but of very intense

brown color. Generally however alkaline decomposition of sucrose requires very high temperatures. Honig (1953) cites as an example that in a solution of sucrose with lime of pH 12 the sugar loss in 1 h of boiling under normal pressure was found to be 0.5%. Since the conditions which the alkaline sucrose solutions were subjected to in this work were much less severe, it is unlikely that any appreciable amounts of sucrose would decompose. Table 11 points out that the pH values of the different solutions remain practically constant throughout the freeze-drying experiment. However it is evident that the pH values of the rehydrated freeze-dried samples are approximately 2 pH units below the values recorded before freeze drying for the most basic samples. It has been mentioned previously that sucrose decomposition is accompanied by the formation of a variety of acids which would have the effect of lowering the solution pH. The rehydrated samples were perfectly clear and showed no discoloration as would be expected if decomposition had occurred. The reason for this decrease in pH for the basic samples after freeze drying remains to be explained. In light of the mild conditions employed in these retention studies it is believed that the sucrose remains unaltered at

all pH levels and does not degrade to form products which may modify retention values.

Hydrogen bonding between sucrose molecules in solution could conceivably be altered by the presence of excess protons or hydroxyl groups. If an increased degree of hydrogen bonding was to take place at high and low pH values, the results of Figures 38 and 39 could be explained by the microregion theory and the selective diffusion theory. According to the microregion theory if hydrogen bonding between sucrose molecules were to be enhanced, more microregions would be formed and increased volatile retention would be expected. On the basis of the selective diffusion theory an increase in hydrogen bonding would have the effect of increasing the viscosity within the CAS region. Since the diffusion coefficients of the volatiles within the CAS would decrease as the viscosity within the CAS increases, volatile retention would increase. Viscosity measurement of 10% sucrose solutions at room temperature showed that the pH had negligible effect on viscosity over the pH range 2.7 to 11.0.

At this point in time the increased retention of volatiles at low and high pH values remains unexplained. It has been shown that the parameters of volatile solu-

bility and solution viscosity are not changed by pH at room temperature. It must be remembered, however, that the freezing of a solution is a concentration process. As water separates as pure ice, the remaining solution will be concentrated in dissolved solids, volatile and protons or hydroxyl ions. Thus the chemical composition of the CAS is far removed from that of the initial solution in which the solubility and viscosity were tested as a function of pH.

Figure 40 illustrates that carvone retention in 10% glucose is similar to the results obtained in sucrose solutions as pH is varied. The carvone retention curve exhibits a minimum near neutrality and increases at high and low pH values. Figure 40 also illustrates that eugenol retention in 10% glucose is constant over the pH range 3 to 7 and then rises as the solution becomes more basic.

Volatile retention in gum arabic solutions of different pH values indicate trends similar to those found with sucrose and glucose as evidenced in Figure 41. Gum arabic is a polysaccharide of molecular weight 240,000-300,000 and contains D-galactose, L-arabinose, L-rhamnose and D-glucuronic acid groups (Furia, 1968). The presence of the D-glucuronic acid residues accounts

for the resultant pH of the solutions being very close to pH 5. It is clearly indicated in Figures 42 and 43 that piperitone and pulegone show behavior similar to that of eugenol and carvone. Figures 42 and 43 also point out that for pH values greater than 5, the degree of volatile retention increases in a steady manner as the pH of the solution is raised.

The chemistry of gum arabic is fairly well documented (Glicksman, 1962). As in the case of sucrose and glucose, there is no indication why retention should increase at high and low pH values in gum arabic solutions. Studies at room temperature have shown that the viscosity of gum arabic solutions is a maximum at pH 6 to 7 (Glicksman, 1969) where volatile retention is close to its minimum value. Studies on systems which approximate conditions found within the CAS would undoubtedly be helpful in determining the effect that pH has on retention in these carbohydrate systems.

In contrast to the dissolved carbohydrate systems, it is apparent that initial pH has little influence on volatile retention in salt solutions. Table 12 illustrates that carvone retention in sodium chloride is practically independent of the solution pH. These results together with the results of the car-

bohydrate-containing systems would suggest that the influence pH exerts on volatile retention is important only for systems where hydrogen bonding is possible.

Figure 22 illustrates that the volatile containing freeze-dried product is very stable even when subjected to a vacuum for long periods of time. Chirife and Karel (1974a) have shown that freeze-dried maltose solutions containing 1-propanol are stable under vacuum at elevated temperatures. These authors have also demonstrated that volatile loss from the freeze-dried matrix is dependent to a large extent on the water activity of the surrounding atmosphere. Figure 44 points out that carvone retention in a freeze-dried sucrose matrix is critically dependent on the moisture content as well. Volatile retention in rehumidified freeze-dried samples has been discussed by Chirife and Karel (1974a) and King and Massaldi (1974). King and Massaldi (1974) developed a diffusion based mechanism to explain the loss of volatiles in rehumidified freeze-dried samples. These authors pointed out that the loss of volatiles may be a function of the thickness of the CAS regions within the freeze-dried samples. The thinner regions lose the volatile more quickly during rehumidification whereas the volatile is kept for a longer period of time within the thicker regions.

F. CONCLUSIONS

The retentions of piperitone, pulegone and carvone (terpenic essential oil components) and eugenol and m-anisaldehyde (non-terpenic essential oil components) were studied during the freeze drying of model solutions. Sucrose, glucose, sodium chloride and gum arabic were used as dissolved solids. The retention level of these sparingly soluble volatiles was enhanced by:

1. an increase in sample thickness
2. an increase in initial dissolved solids content
3. a reduced initial volatile content
4. an increase in the freezing rate
5. acidic or basic conditions
6. the absence of additional sparingly soluble volatiles

It is apparent that the behavior of the sparingly soluble essential oil components parallels that of infinitely soluble volatiles to some extent. However, as shown by experiments on the freezing rate and sample thickness, differences do exist as the two classes of volatile exhibit different retention characteristics. Because liquid food concentrates contain both soluble and relatively insoluble flavoring components, processing conditions must be regulated to give maximum retention of

the different types of volatile. The organoleptic quality of a rehydrated freeze-dried food is directly related to the concentrations of the volatile flavoring compounds.

Massaldi and King (1974a) have warned that the practice of adding flavoring components to a food concentrate before freeze drying may not be advantageous. The results using octanol as an additional volatile show that the presence of an additional sparingly soluble volatile adversely effects the degree of volatile retention.

The fact that the solution pH tremendously influences the degree of volatile retention is very interesting. The implications of these findings are at once recognizable. If a liquid food could be successfully acidified, the retentions of the volatile flavoring compounds would be increased, hence the quality of the rehydrated product would more closely match that of the original liquid food.

In most cases, the degree of volatile retention can be rationalized on the basis of the selective diffusion theory or the microregion concept. Volatile retention by the adsorption mechanism is seen to play only a minor role.

III. Solution Properties of Terpenic Essential Oil Components

A. INTRODUCTION

Recent studies, involving the retention of flavoring organic compounds during the freeze drying of aqueous solutions, have shown that the degree of solubility of the flavoring compound has a pronounced effect on volatile retention (Flink and Gejl-Hansen, 1972, Flink et al., 1973 and Massaldi and King, 1974a).

Solubility data for many of the important sparingly soluble flavoring compounds is scarce. The essential oil components, both terpenic and non-terpenic, remain relatively unexplored even though these compounds are commonly used in the preparation of non-alcoholic beverages, ice creams and ices (Hall and Oser, 1968). Thus an investigation was initiated to determine the solubility parameters of pulegone, piperitone and carvone in sucrose, glucose and sodium chloride solutions of varying solids concentration. The solubility studies were carried out at temperatures of 10, 20 and 30°C with a view to exploring some thermodynamic properties of the saturated solutions.

B. LITERATURE REVIEW

1. Techniques for Determining the Solubility of Liquids in Liquids

Since solubility measurements in liquid-liquid systems do not require experimentation of any great complexity, the variety of experimental designs is not large. Classical techniques such as the volume method and the cloud point method, as reviewed by Zimmerman (1951), are very useful in the determination of mutual solubilities of various organic compound-water mixtures (Hill, 1923, Hill and Malisoff, 1926 and Ginnings and Baum, 1937).

At the present time instrumental methods are most widely used as analytical tools in the determination of mutual solubilities of liquids. Gas-liquid chromatography has proven to be very suitable for solubility studies. McAuliffe (1966) obtained solubility values of paraffins, cycloparaffins, olefins, acetylene, cycloolefins and aromatic hydrocarbons in water using the glc technique. Buttery et al. (1969) used glc to determine the solubilities of alkanals, alkan-2-ones and methyl alkanoates. The technique employed in these two studies consisted basically of saturating water with

the desired organic compound and then letting the two phases separate. The saturated aqueous phase was analyzed by glc and saturation concentrations were determined by comparison with standard solutions. Sutton and Calder (1975) modified the approach somewhat by extracting the hydrocarbon dissolved in water with a non-interfering organic solvent. Massaldi and King (1973) determined aqueous solubilities of n-hexyl acetate, n-butylbenzene and d-limonene using a head-space type of analysis. The head-space technique had the advantage of not requiring phase separation of saturated solutions. In general solubility measurements by glc offer several distinct advantages. Impurities are of no significance if their peaks do not interfere with the measurement of the desired hydrocarbon peak. In addition very high sensitivities are attainable especially with flame ionization detectors.

Spectrophotometric techniques have proven useful in the determination of solubilities of various aromatic hydrocarbons in water. In particular ultra-violet spectrophotometry has been very useful in monitoring unsaturated compounds. Andrews and Keefer (1950) investigated the solubilities of substituted benzenes in water and aqueous silver nitrate at 25°C. Samples

of the saturated solution were extracted with hexane and the resultant hexane solutions were analyzed spectrophotometrically. Bohon and Claussen (1951) used both a non-extractive and a n-heptane extractive procedure to study the solubility of substituted benzenes in water. Wauchope and Getzen (1972) employed the ultraviolet method in a temperature study of the solubilities of solid aromatic hydrocarbons in water. The ultraviolet technique suffers from the disadvantage of being suitable only to those compounds which exhibit strong absorptions within the ultraviolet region of the spectrum.

A non-instrumental method worthy of mention is that developed by Sobotka and Kahn (1931). This technique involves the dispersion of a water-insoluble dye (Sudan IV) into large amounts of water or aqueous solution and adding the organic compound in small increments using a microburet. When the aqueous sample is saturated with the organic compound, the excess organic appears as immiscible red liquid droplets as the excess organic dissolves the dye. This technique still finds application at the present time as evidenced by the work of Sada et al. (1975) who studied the solubilities of toluene in aqueous salt solutions.

2. Properties of Dilute Aqueous Solutions

Aqueous solutions, which are saturated with a sparingly soluble compound, may be considered as being infinitely dilute. Thus solubility values of relatively insoluble compounds allow for the evaluation of thermodynamic parameters for solutions at infinite dilution.

Rowlinson (1969) has segregated nonelectrolytes into two classes. Typically aqueous solutes are those which exhibit in aqueous solution such anomalous thermodynamic properties as found only in aqueous systems. Typically aqueous solutes are subdivided into two classes, apolar solutes and mixed solutes. Apolar solutes, as the name suggests, contain no polar groups and would include pure hydrocarbons and the inert gases. Mixed solutes are those which contain a large apolar region and a polar group. Alcohols, ketones, amines and ethers are examples of species which would be included within the mixed category. Typically nonaqueous solutes are those which have aqueous solution properties similar to those of normal nonaqueous solutions. Glucose, sucrose and other sugars are prime examples of typically nonaqueous solutes.

Dilute aqueous solutions of typically aqueous solutes have received a great deal of attention within

the past few years. Thermodynamic data obtained from solubility studies or calorimetric experimentation has shown that water is a unique solvent in that it exhibits properties not found in any other solvent. All of the typically aqueous solutes such as the inert gases (Alexander, 1959), hydrocarbons (Nemathy and Scheraga, 1962), alcohols (Franks and Reid, 1973), cyclic ethers (Cabani et al., 1971a), amines (Franks and Watson, 1969) and ketones (Gross et al., 1939) were found to possess very highly negative partial molar entropies of hydration, ΔS_h, (h subscript refers to the process, pure solute (ideal vapor)→solute (solution) whereas s subscript refers to the process, pure solute (liquid)→solute (solution)). In addition the aqueous solubilities of most typically aqueous solutes were found to decrease with increasing temperature. The molar heat capacities of such solutions are also large and positive.

Various theories have been advanced to account for the unusual properties exhibited by aqueous solutions of typically aqueous solutes. The starting point for the most advanced and sophisticated water theories is the "iceberg" model which was proposed by Frank and Evans (1945). This iceberg model supposes that pure water is a mixture of distinguishable molecular species which

are in a state of equilibrium. $(H_2O)b$ is termed bulky

$$(H_2O)b \rightleftharpoons (H_2O)d$$

water and it is a species which is extensively hydrogen bonded with predominantly four fold coordination (as in ice) and therefore possesses a low density. $(H_2O)d$ is termed dense water as it contains nonbonded OH groups such that the O-O distances are shorter than the normally accepted hydrogen bond lengths and therefore possesses a higher density. Frank and Evans (1945) labelled the ordered water structures, $(H_2O)b$, as "icebergs" since the properties of $(H_2O)b$ have been identified with those of ice. The presence of an apolar solute or the apolar region of a mixed solute in water is believed to shift the above equilibrium to the left i.e. toward the more structured form of water. Thus the number of icebergs increases when a typically aqueous solute is placed in water. This equilibrium shift to the more ordered water structure accounts for highly negative ΔS values as typically aqueous solutes are dissolved in water. Highly negative entropies are a sign of ordering or loss of randomness within a system, with the $(H_2O)d$ species being the less ordered form of water. Solubilization of

an apolar solute or a mixed solute occurs when the solute molecules occupy a cavity or partial cavity within the $(H_2O)b$ cluster. The ability of the guest molecule to occupy a cavity within the $(H_2O)b$ host is dependent upon the size of the guest molecule and it has been shown that there exists an optimum molecular diameter for maximum solubility (Franks and Reid, 1973).

Many solutes, which may be considered as typically aqueous, exhibit decreasing solubilities in water with an increase in temperature. Compounds such as ketones (Gross et al., 1939), n-butyl alcohol (De Santis et al., 1976), butane (Rice et al., 1976), ethyl ether and isoamyl alcohol (Kablukov and Malischeva, 1925), ethyl acetate (Glasstone and Pound, 1925), isomeric pentanols (Ginnings and Baum, 1937) and aliphatic ethers (Bennett and Phillips, 1928) have lower solubilities at higher temperatures. In a sense the solubility characteristics of liquid organics appear to parallel the well known solubility characteristics of gases.

The explanation for this decrease in solubility with an increase in temperature comes from considering the effect that elevated temperature has on the iceberg. According to the iceberg model, the $(H_2O)b$ species acts as a host for the solutes. An increase

in temperature has the effect of decreasing the number of $(H_2O)b$ species (melt the icebergs!) and thus shifts the equilibrium in favor of the $(H_2O)d$ species. Thus at higher temperatures, the number of host clusters is lower and the solutes are less soluble.

In contrast to the above examples several organic species do not exhibit an increased solubility with lower temperatures. Wauchope and Getzen (1972) have shown that the solubilities of solid aromatic hydrocarbons increase as the temperature is increased. d-Limonene was also found to have higher solubilities at higher temperatures (Massaldi and King, 1973). Bohon and Claussen (1951) noted that many aromatic hydrocarbons exhibited a solubility minimum at 18°C and identified this solubility minimum with a heat of solution being equal to zero.

It is well known that the presence of a dissolved solid (ionic or nonionic) in water may significantly reduce the solubility of a liquid organic species (Rice et al., 1976 and Massaldi and King, 1973). Many authors currently hold the opinion that this salting out effect is due to the added solute becoming hydrated in solution so that the molecules of water involved in the hydration are no longer available for dissolution

of the second substance, thus the solubility of the second substance is reduced. Many years ago Glasstone and Pound (1925) questioned this concept and concluded, on the basis of calculated hydration values, that other more important factors were operative in the salting out effect.

The ability of different types of sugars and salts to reduce the solubility of typically aqueous solutes in water has been investigated from the viewpoint of the iceberg model of water. Ben-Naim (1965a, 1965b and 1967) has studied the solubilities of the apolar solute, argon, in aqueous solutions containing an additional component. In solutions containing methanol, ethanol, n-propanol and n-butanol, the solubility of argon was found to be higher than the solubility in pure water. These alcohols fall within the mixed category of solutes and are considered to be solutes which increase the structural integrity of water. The solubility of argon decreased in aqueous solutions of glucose, sucrose, glycerol and simple electrolytes. Ben-Naim concluded that these hydrophilic solutes decreased argon solubility by decreasing the structural integrity of water i.e. reduced the number of host $(H_2O)_b$ species. Franks (1973) has criticized Ben-Naim's explanation and

Franks (1973) maintains that molecules of glucose in aqueous solution are surrounded by $(H_2O)b$ species and that glucose is in fact a promoter of water structure. In this case the hydroxyl groups of glucose are accommodated into the structured water. The fact that glucose reduces the solubility of typically aqueous solutes in aqueous solution indicates that the hydration of glucose and argon are incompatible. At the present time the exact mechanism of this salting out effect is still under investigation. Franks and Reid (1973) warn that extreme caution must be exercized when one attempts to explain interactions in ternary systems.

C. EXPERIMENTAL

1. Materials and Chemicals

d-Glucose (Fisher), sucrose (Baker) and sodium chloride (MCB) were used as received. Carvone (K and K), piperitone (ICN), and pulegone (Fluka) were used as received. Analysis by gas chromatography revealed these compounds to be at least 90% pure. All solutions were prepared with distilled water.

2. Equipment

Saturated solutions were prepared in a Labline Environmental Chamber (Labline, Inc.) and temperatures are accurate to ±0.2°C. A Vortex-Genie (Scientific Industries, Springfield, Mass.) was used to mix the aqueous solution with the added organic species. Separation of the saturated aqueous layer from excess organic was accomplished on a Janetzki T5 Centrifuge (Heinz Janetzki Kg.) which was equipt with a fixed angle rotor. Ultraviolet absorption measurements were conducted on a Unicam SP1800 Ultraviolet Spectrophotometer (Pye Unicam). The instrument was operated on the fixed wavelength mode using a band width of 1.2 mm and a slit width of 0.4 mm. Quartz cells (Canlab) were used for reference and sample during ultraviolet analysis.

3. Preparation of Standard Curves

Standard solutions of the organic species in water were prepared so that the range of absorbances for the standard solutions fell between 0.4 and 1.4. It has been found that absorbances falling within this range are the most reliable for double beam spectrophotometers (Willard et al., 1965). The standard curves for carvone (Figure 45), pulegone (Figure 46) and piperi-

tone (Figure 47) illustrate that the Beer-Lambert Law is valid for absorbances between 0 and 1.2. Values of log ε, the extinction coefficient, were calculated from the slope of the standard curve and are tabulated in Table 15 together with previously measured values of log ε in ethanolic solution.

4. Preparation of Saturated Solutions and Solubility Determinations

All saturated solutions were prepared in a Labline Environmental Chamber (±0.2°C). Conical 12 ml centrifuge tubes with screw tops were filled with 8.0 ml of aqueous solution. Approximately 0.1 ml of the organic species was added. The contents of the centrifuge tubes were mixed on the vortex mixer for 8 min. After mixing the tubes were centrifuged for as long as was required to effect separation between excess organic and the aqueous phase. In some cases centrifugation times of several hours was required. The centrifugation was carried out at the temperature at which the saturation was performed. When centrifugation was completed, as evidenced by a totally clear aqueous phase, a 1 ml graduated pipet with a teflon extension was used to remove aliquots from the aqueous phase. To insure that

none of the less dense organic phase entered the pipet, a gentle blowing action was applied as the teflon tip passed through the organic layer. After the 1 ml aliquot had been withdrawn from the centrifuge tube, the teflon tips were removed and the contents of the pipet were emptied into a suitable volumetric flask and diluted with water. The absorbance of the diluted saturated solution was measured and the concentration of the organic species was determined from the previously obtained standard curves.

Various tests were performed to insure that the above technique produced saturated solutions. Eugenol was chosen as the test component because it was observed that during the preparation of the standard solutions eugenol required the longest times and most vigorous shaking for dissolution in water. For example in the preparation of standard eugenol solutions, vigorous shaking for at least 15 min was required to dissolve 0.05 g of eugenol in 500 ml water (1/20 th saturation concentration). At room temperature saturated solutions of eugenol in 30% glucose were prepared by vortex mixing for 3, 5, 7 and 9 min. 1 ml aliquots were withdrawn after centrifugation and suitably diluted. The respective measured absorbances were 0.378, 0.384,0.377

and 0.378. Thus it was concluded that the 30% glucose solution was saturated with eugenol within 3 min of vortex mixing. It was also shown that the concentration of the organic species in the aqueous phase did not increase with increased contact time between the aqueous phase and the excess organic. For example, at 10°C the solubility of pulegone in 40% glucose was found to be 0.655±0.008 g/l immediately after vortexing. The saturated pulegone samples were allowed to stand for 48 h at 10°C in contact with excess pulegone and then remixed. The pulegone concentration after this period was found to be 0.659±0.007 g/l. In a similar test, the saturation concentration of piperitone, after vortexing a 15% sodium chloride solution at 10°C was 0.677±0.011 g/l. After six days the concentration was found to be 0.675±0.005 g/l. Hence on the basis of these tests it was concluded that the aqueous solutions were saturated with the organic species during vortex mixing.

5. Evaluation of Thermodynamic Parameters

a) Activity Coefficients

The activity coefficients, γ, for piperitone, pulegone and carvone in aqueous solution were calculated

according to Henry's Law which is depicted in Equations 1

$$p = p^{\circ}\gamma X \qquad (1a)$$

$$p = \frac{p^{\circ}X}{Xs} \qquad (1b)$$

where p is the partial pressure of solute above the solution, X is the mole fraction of solute in solution, p° is the vapor pressure of the pure solute and Xs is the solubility of the solute in the aqueous solution expressed as a mole fraction. At saturation, p equals p° (X=Xs) and thus γ is defined by the term 1/Xs. p° values (Pa) for piperitone, pulegone and carvone were determined at 10, 20 and 30°C from existing vapor pressure data (Handbook of Chemistry and Physics, 1969).

b) Partial Molar Free Energies

Partial molar free energies of hydration, ΔGh, were derived by Equation 2. As outlined in Appendix 4

$$\Delta Gh = RT\ln\frac{p}{Xs} \qquad (2)$$

ΔGh is the defined as the difference in chemical potential between the solute at infinite dilution in aqueous solution and the solute as an ideal vapor. The subscript h

refers to the process, solute (ideal vapor) → solute (solution).

Partial molar free energies of solution, ΔGs, were derived using Equation 3 with a knowledge of ΔGh (Cabani et al., 1971b). The subscript s refers to the

$$\Delta Gh = \Delta Gs + RT\ln p^{\circ} \qquad (3)$$

process, solute (pure liquid) → solute (solution). p° values are defined in terms of Pascals.

c) Partial Molar Enthalpies

Partial molar enthalpies of solution, ΔHs, were obtained from plots involving Equation 4 which is derived in Appendix 5. ΔHs is defined as the enthalpy difference

$$\frac{\partial \ln \gamma}{\partial \frac{1}{T}} = \frac{\Delta Hs}{R} \qquad (4)$$

between the solute in saturated aqueous solution and pure liquid solute.

Partial molar enthalpies of hydration, ΔHh, were determined using Equation 5 with a knowledge of ΔHs

values (Franks et al., 1970). ΔHv values (latent heat of

$$\Delta Hs = \Delta Hh + \Delta Hv \qquad (5)$$

vaporization) for piperitone, pulegone and carvone were calculated at 10, 20 and 30°C using the Watson correlation (Reid and Sherwood, 1966) and ΔHvb values were obtained using the Reidel empirical method (Reid and Sherwood, 1966).

Partial molar entropies of hydration and solution ΔSh and ΔSs respectively, were calculated from Equation 6 (Wall, 1965).

$$\Delta G = \Delta H - T\Delta S \qquad (6)$$

D. RESULTS

Solubility data for piperitone in aqueous solutions of sucrose, glucose and sodium chloride is given in Table 16. Generally the solubilities, expressed as g/l solution, are precise to ±1% as expressed in terms of the relative standard deviation. Two main trends are evident in Table 16. Firstly, the solubility of piperitone in the aqueous solutions decreases as temper-

ature increases. Secondly, the solubility of piperitone invariably decreases as dissolved solid content increases. It is apparent that the ability of the dissolved solid to decrease the piperitone solubility follows the order, sodium chloride > glucose > sucrose. Table 16 shows that for each of the dissolved solids at 0 wt% a solubility value is given. Since solubilities for the different dissolved solids were carried out at different times, a water solubility test was carried out with each dissolved solid to insure that factors involving instrumentation and technique remained invariant.

Solubility data for pulegone is tabulated in Table 17. Although the solubility of pulegone was found to be close to one half the value obtained for piperitone, the solubilities, as influenced by temperature and dissolved solids content, followed trends similar to piperitone.

Carvone solubility, as shown in Table 18, was found to reach a minimum value between 10 and 30°C as evidenced by the lowest solubility value at 20°C. Table 18 also illustrates that carvone solubility decreases as the dissolved solid content increases.

Tables 19, 20 and 21 illustrate calculated activity coefficients, γ, for piperitone, pulegone

and carvone respectively. Figures 48, 49 and 50 depict ln γ as a function of dissolved solids content expressed as wt%. Generally for the compounds piperitone and pulegone, γ tends toward higher values with an increase in temperature at any dissolved solids content. At a constant temperature γ for pulegone (Figure 49) and piperitone (Figure 48) are seen to increase with increasing dissolved sodium chloride and glucose contents. γ values for pulegone and piperitone in sucrose solutions do not appear to follow the same trends found in the glucose and sodium chloride solutions. At 10°C both pulegone and piperitone γ values show a definite increase with dissolved sucrose content, whereas at 20°C the γ for both compounds appears to be independent of sucrose content. At 30°C γ for piperitone decreases slightly with increased sucrose whereas pulegone shows a more pronounced decrease between 40 and 50% sucrose.

As shown in Figure 50, the effect of the different dissolved solids on the γ for carvone is quite similar to that previously found for pulegone or piperitone. Once again sodium chloride content has the greatest influence on γ, followed next by glucose and sucrose.

Tables 22 through 30 show the calculated

thermodynamic values for piperitone, pulegone and carvone in aqueous solutions containing sucrose, glucose or sodium chloride. Several trends are at once evident. ΔHh and ΔHs values for piperitone (Table 22), pulegone (Table 25) and carvone (Table 28) generally become more positive with increasing temperature at a constant dissolved solids content. At a constant temperature ΔHh and ΔHs appear to become more positive with increasing dissolved solids content in most cases. However, ΔHh and ΔHs for the sodium chloride solutions appear very erratic. Since ΔHs values were calculated from a plot of $\ln \gamma$ vs. $1/T$, the experimental errors incurred in the measurement of γ will be greatly magnified, hence the ΔHs values will inherently have a high degree of uncertainty. In addition, ΔHh values will be approximate because of the empirical expressions used to calculate ΔHv. Thus any discussion of ΔHs or ΔHh must be restricted to general trends.

ΔGh and ΔGs values for piperitone (Table 23), pulegone (Table 26) and carvone (Table 29) invariably increase with increasing temperature at a constant dissolved solids content. In all three cases values of ΔGh and ΔGs appear to be relatively independent of dissolved sucrose or glucose. Increased sodium chloride concen-

trations, however, are seen to increase ΔGh and ΔGs values at constant temperature.

ΔSh and ΔSs values for piperitone (Table 24), pulegone (Table 27) and carvone (Table 30) generally become more positive with increasing temperature at constant dissolved solids content however it is evident that exceptions do exist. Since ΔSh and ΔSs values were obtained from a differentiation procedure involving γ, the experimental errors incurred in the determination of γ will be magnified, hence some erratic behavior in the entropy terms is expected.

F. DISCUSSION

The iceberg model of water solutions was invoked by Frank and Evans (1945) to explain the unusual thermodynamic properties of aqueous solutions, especially those involving enthalpies and entropies. Values of ΔHs (the heat associated with the transfer of one mole of solute as a pure liquid to an aqueous solution at infinite dilution) are preferably derived by calorimetric techniques. The use of a calorimetric technique obviates the use of γ to find ΔHs and thus errors in γ are not magnified in the computation process. ΔHh is the preferred thermodynamic parameter used by most authors (Franks and Watson, 1969) and is related to ΔHs by ΔHv, the latent heat of vaporization. ΔHh reflects total solute-solvent interactions because solute-solute interactions in the vapor state are considered negligible (the vapor is considered an ideal gas). ΔHs values, on the other hand, reflect the difference between solute-solute and solute-solvent interactions because the pure liquid solute is chosen as the standard state. Owing to the complexity of the solute-solute interactions in the pure liquid state, the hydration parameters are preferred since solute-solute interactions need not be considered.

Figure 51 illustrates the curves relating γ and T used for the evaluation of ΔHs for piperitone, pulegone and carvone in pure water. Values of ΔHs are derived at any temperature by computing the slope of the curve at that temperature. Values of ΔHh, tabulated in Tables 22, 25 and 28 for piperitone, pulegone and carvone respectively show that the process of transferring one mole of solute from the ideal vapor to a solution at infinite dilution (mole fraction of solute at saturation is approximately 10^{-4}) is an exothermic process i.e. heat is evolved. The overall magnitude of ΔHh is determined from the contributions of two mechanisms. A positive heat (endothermic) corresponds to the heat required to form a cavity for the solute molecule to occupy. A negative heat (exothermic) results from the formation of a more ice-like water structure i.e. icebergs. Obviously the formation of a more ordered form of water is the main contribution to ΔHh. It is interesting to note that the ΔHh values for cyclic ethers (Cabani et al., 1971b and Franks et al., 1970), dialkylamines (Franks and Watson, 1969) and the three compounds of this study all fall within the range -50000 to -70000 $Jmole^{-1}$.

Tables 22, 25 and 28 indicate that the respective

ΔHh values for piperitone, pulegone and carvone become less negative with an increase in temperature. Several previous studies have shown similar results. Gross et al. (1939) noted that ΔHh for many aliphatic ketones became less negative with increased temperatures in the range 0 to 50°C. ΔHh for cyclic ethers (Franks et al., 1970) and dialkylamines (Franks and Watson, 1969) were found to exhibit exactly the same tendency in pure water. Again the model of the iceberg may be used to rationalize the less negative ΔHh values at higher temperatures. More positive ΔHh values indicate that at higher temperatures the heat capacities, ΔCp, are higher. A larger value of ΔCp at higher temperatures is a direct consequence of the "melting" of a greater number of iceberg species at the higher temperature.

Figure 51 and Table 28 illustrate that at a temperature very near 20°C, ΔHs for carvone has a value of zero. When ΔHs=0, the negative heat due to increased ordering in water exactly balances the positive heat of cavity formation. Figure 51 shows that the pulegone and piperitone curves are quickly approaching a maximum similar to that shown by carvone. According to Bohon and Claussen (1951) the temperature at which ΔHs=0 corresponds to the point of minimum solubility of the solute in water.

Tables 22, 25 and 28 indicate that the presence of dissolved solids has the general effect of making the ΔHh values more positive at constant temperature. These results lend support to the theory of Ben-Naim (1965a, 1965b and 1967) who has defined glucose, sucrose and ionic salts as water structure breakers. More positive ΔHh values with increasing dissolved solids content indicates that there are less $(H_2O)b$ species formed hence the contribution of the negative heat (due to the formation of ice-like water) is much less.

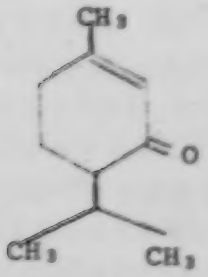
ΔGh values for piperitone (Table 23), pulegone (Table 26) and carvone (Table 29) in water appear to be very similar in magnitude. In addition, at a constant temperature, ΔGh, appear to be practically constant in water and aqueous solutions of sucrose and glucose. Only increasing concentrations of sodium chloride appear to have any significant effect on ΔGh. In most cases the values of ΔGh are seen to increase with an increase in temperature (at constant dissolved solids content). Similar observations were made for aliphatic ketones (Gross et al. 1939). As shown in Tables 23, 26 and 29, values of ΔGs are invariably lower than ΔGh. The relative magnitude of ΔGh and ΔGs are determined by the units of p° in the expression $\Delta Gh = \Delta Gs + RT\ln p°$.

In this study, p° was expressed in terms of Pascals hence the RTlnp° term is always positive. Cabani et al. (1971a) expressed p° values in terms of atmospheres, hence the calculated ΔGh values were less than ΔGs values.

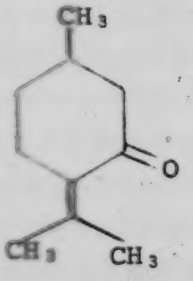
The partial molar entropies of hydration and solution, ΔSh and ΔSs respectively are of considerable interest since their values reflect the degree of ordering or structure within the solution. ΔSh values for piperitone (Table 24), pulegone (Table 27) and carvone (Table 28) in water are seen to be highly negative. Such highly negative values of ΔSh point out that the solubilization of piperitone, pulegone or carvone brings about a less random or more ordered state within the solution i.e. formation of a greater number of $(H_2O)b$ species. It is also evident that values of ΔSh generally appear to become less negative as dissolved solids content increases at a constant temperature. This effect of increasing dissolved solids to reduce the order within the solution again lends support to the theory of Ben-Naim (1965a, 1965b and 1967) who considers such dissolved solids as structure breakers.

The solubility data presented in Tables 16, 17 and 18 show that the solubilities of the essential oil components are quite low and explains why such compounds

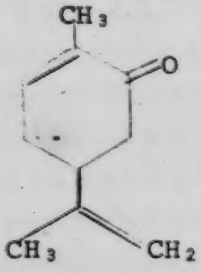
have generally been considered as insoluble. It is remarkable that the three compounds, piperitone, pulegone and carvone, which are very similar in structure, should have different solubilities. In particular piperitone solubility is twice that of carvone or pulegone. A



piperitone



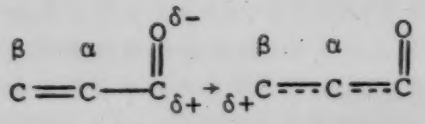
pulegone



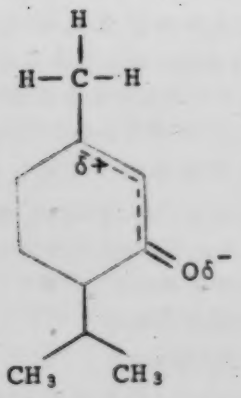
carvone

possible explanation for the higher solubility of piperitone over that of pulegone may be found by consideration of the electronic structures in a method analogous to that of Palit (1947). According to Palit (1947) the doubly-bound oxygen in the carbonyl group shows an electromeric effect in that it serves as a sink for electrons, C=O. Thus the electron density on the carbonyl carbon atom is reduced and this carbon atom acquires a partial positive charge. In saturated ketones or aldehydes, the loss of electrons from the carbonyl carbon may be partially replenished by a flux of electron density from neighbouring C-H bonds.

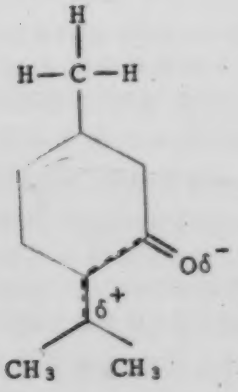
As the electron density is decreased in the C-H bond, this bond will become polarized with the hydrogen atom becoming slightly positive in character, $C\text{-}H^{\delta+}$. It is the degree of polarization of C-H linkages which determines the solubility of aldehydes or ketones as the partially positive hydrogen atoms are able to interact with water by hydrogen bonding. It is well known that the C-H linkages on methyl groups are especially susceptible to this type of polarization as evidenced by the infinite solubility of acetone (CH_3COCH_3) and acetaldehyde (CH_3CHO). A similar, but different situation would prevail for the α, β unsaturated ketones. In this case the π electrons of the double bond would serve as the main electron source for the electron deficient carbonyl carbon atom. As a result the β carbon



would acquire a partial positive charge since the electron density between the α and β carbon atoms has been diminished. In the case of piperitone and pulegone, the following intermediate structures may be envisioned.



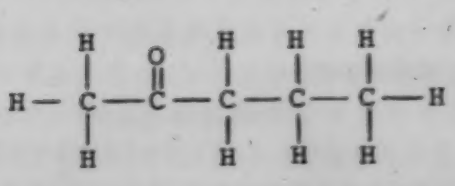
piperitone



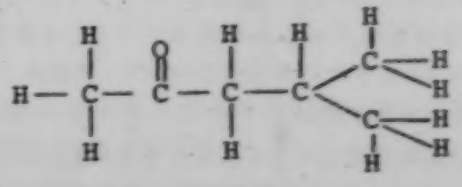
pulegone

In both cases the carbon atom, β to the carbonyl carbon, has acquired a partial positive charge. In piperitone this partially positive β carbon is adjacent to a methyl group and a CH_2 group within the ring whereas in pulegone the β carbon is adjacent to two methyl groups. At this point the excellent electron releasing abilities of the methyl groups come into play. In piperitone electron density from the lone methyl group will act as an electron source to replenish negative charge on the β carbon thus inducing a polarized C-H bond. Similarly in pulegone, the two methyl groups will act as an electron source for the β carbon, but in this

case the polarization of the C-H bonds will be significantly less than the polarization of the C-H bonds in piperitone due to the fact that each methyl group of pulegone will donate only a fraction of the total negative charge to the β carbon. As stated previously the presence of strongly polarized C-H bonds in a methyl group is of the utmost importance in determining the solubility of an aldehyde or ketone in water. Moreover, it is probably true that the presence of one methyl group in which the C-H bonds are strongly polarized confers greater solubility than that of two methyl groups in which the C-H bonds are less strongly polarized as in piperitone and pulegone respectively. Solubility studies on aliphatic ketones (Gross et al., 1939) give qualitative support to these arguements. The solubilities of methyl n-propyl ketone and methyl isobutyl ketone were found to be 0.630 and 0.166 moles per 1000 g of water. As indicated by their structures, a rough analogy



Methyl n-propyl ketone



Methyl isobutyl ketone

can be made between the structures of piperitone and methyl n-propyl ketone, and pulegone and methyl isobutyl ketone.

An alternate more thermodynamically based explanation for the observed solubilities of piperitone, pulegone and carvone is derived from considering the iceberg model of water. The guest molecule or solute occupies a cavity or partial cavity within the $(H_2O)b$ cluster. The ability of the guest molecule to occupy a cavity is dependent on the size of the guest molecule and it has been shown that there exists an optimum molecular diameter for maximum solubility (Franks, 1973). If it can be assumed, that in piperitone, pulegone and carvone, the carbonyl-water interactions are similar (the carbonyl has two proton acceptor sites) then the difference in the solubilities of these compounds may be due to the difference in the molecular diameter of the molecules. It is evident that pulegone and carvone will have different diameters than piperitone since the former compounds both possess unsaturated isopropyl groups outside of the six-membered ring whereas piperitone does not. The presence of this unsaturated isopropyl group may render the molecular structure incompatible with the structure of the cavity, hence carvone and pulegone

exhibit lower water solubilities. Piperitone, on the other hand, may not be sterically hindered to such a great extent so as to prevent inclusion into a water cavity.

Piperitone (Table 16) and pulegone (Table 17) display decreased solubilities in water with higher temperatures. This behavior, as discussed previously, is followed by very many liquid organic compounds in aqueous solution. An explanation for a decreased solubility with an increase in temperature can be found, once again, by considering the iceberg model of water. The $(H_2O)b$ species, which exists in equilibrium with $(H_2O)d$, has many characteristics that have been likened to ice. An increase in temperature has the effect of decreasing the number of $(H_2O)b$ species, i.e. decrease the number of host species for the solute. Thus the consequence is lower solubilities at higher temperatures.

Of the three compounds studied, carvone is unique in that it exhibits a solubility minimum between 10 and 30°C as seen in Table 18. Bohon and Claussen (1951) noted a similar solubility minimum for aromatic hydrocarbons in water. Bohon and Claussen (1951) correlated this solubility minimum with the temperature at which the heat of solution became equal to zero.

Figure 51 shows that ΔHs values for piperitone and pulegone will similarly equal zero at a temperature slightly higher than 30°C.

The activity coefficients, γ, for piperitone, pulegone and carvone in saturated aqueous solutions are tabulated in Table 19, 20 and 21 respectively. γ values were derived on the basis that at saturation, the vapor pressure of the dissolved solute approachs that of the pure solute ($ps=p°$) hence γ is equivalent to $1/Xs$. On the basis of the low mole fraction (approximately 10^{-4}) of the volatile solute in the saturated solution, and from the work of Nawar (1971), it was assumed that the term γXs was close to unity in all aqueous solutions.

γ values for piperitone (Table 19), pulegone (Table 20) and carvone (Table 21) are represented graphically as a function of dissolved solids content in Figures 48, 49 and 50 respectively. The high values of γ for the three compounds in water reflect the fact that these solute molecules are not comfortable within their aqueous environment due to unfavorable interactions between the large apolar segment of the solute molecule and the very polar water molecules. Figure 48 and 49 illustrate that increased sodium chloride and glucose contents result in increased values of γ for piperitone

and pulegone. It is apparent that sodium chloride has by far the greatest influence on γ. Bomben et al. (1972), using the data of Glasstone and Pound (1925), showed that γ for ethyl acetate was also extremely sensitive to sodium chloride concentrations. The addition of inorganic salts to increase the vapor pressure of volatile components in dilute aqueous solution is often applied in headspace aroma analysis (Nelson and Hoff, 1968). The effect of the salt is to reduce the solubility of the volatile solute in the aqueous solution and thus increase the amount of volatile solute in the vapor above the solution. Nawar (1966) reported that added glucose also had the ability to increase the vapor pressure of dilute volatile solutes but the increase in the headspace concentration of the volatile was significantly less than when inorganic salts were added.

Inspection of Figures 48, 49 and 50 illustrate that the influence of increased sucrose contents is variable. Piperitone (Figure 48) and pulegone (Figure 49) exhibits slightly increased values of γ with increasing sucrose content at 10°C. At 20°C γ for piperitone and pulegone appear to be relatively independent of dissolved sucrose. At 30°C γ for these compounds appears to decrease slightly. Massaldi and

King (1973) and Chandrasekaran and King (1971) have shown that sucrose in solution increases the γ of highly oxygenated volatiles at 20°C whereas non-oxygenated volatiles show a decrease in γ with increasing sucrose concentrations. The ability of dissolved sucrose to selectively differentiate between different species of volatile solutes partly explains the work of Wientjes (1968) who found that when sugars were added to synthetic strawberry mixtures, some of the volatile components were forced out of the aqueous solution more than others.

Figures 48 and 49 illustrate that temperature as well as dissolved solids has an effect on γ. For the compounds piperitone and pulegone, γ is seen to invariably increase with increasing temperature. Bomben et al. (1972) described a similar trend for ethyl acetate. Owing to the solubility minimum exhibited by carvone (Table 16) near 20°C, γ for carvone will attain a maximum value near 20°C and decrease at higher and lower temperatures. Massaldi and King (1973) noted that γ for d-limonene and n-butyl benzene decreased with increasing temperature and probably suggests that in the temperature range 0 to 25°C, Massaldi and King (1973) were working on the high temperature side of the minimum in d-limonene and n-butylbenzene solubility.

F. CONCLUSIONS

The solubility studies of piperitone, pulegone and carvone in water and aqueous solutions of sucrose, glucose and sodium chloride have provided a great deal of valuable information regarding the behavior of volatile flavoring compounds in dilute aqueous solution.

Enthalpies, entropies and free energies, which were calculated from solubility data at 10, 20 and 30°C, appear to be in good agreement with the iceberg model of water as proposed by Frank and Evans (1945). This study shows that the solution behavior of dilute volatile components can be successfully described in terms of thermodynamic parameters and it is expected that the use of such thermodynamic quantities will help to clarify the nature of volatile solvent interactions in other systems.

Of particular interest to the processor is the fact that the solubility of many sparingly soluble compounds increases with a decrease in temperature. This phenomena at once becomes relevant in processes employing low temperatures, e.g. freeze drying. On the basis of the studies by Ben-Naim (1965a) it appears possible to increase the solubility of a sparingly soluble volatile by incorporating additional structure making volatiles.

Table 1. Diffusion Coefficients of Sucrose at 25°C ($m^2/s \times 10^{10}$);
$\bar{c}$ = 1.000g/100ml, Δc = 2.000g/100ml

Run	Dexp	Dav	Davo	Dlit[d]	Deviation(%)
1[a]	5.16				
2[a]	5.17	5.20±0.06[a]			
3[a]	5.27				
4[b]	5.20				
5[b]	5.24	5.20±0.04[b]	5.19±0.05	5.148±0.005	0.8
6[b]	5.16				
7[c]	5.20				
8[c]	5.10	5.15±0.005[c]			
9[c]	5.15				

a) 5,000 rpm
b) 15,000 rpm
c) 10,000 rpm
d) Diffusion coefficient of sucrose; $\bar{c}$ = 1.011g/100ml, Δc = 1.5016g/100ml and T = 24.95°C (Gosting and Morris, 1949)

Table 2. Variation of Sucrose Diffusion Coefficients ($m^2/s \times 10^{10}$) with Temperature; $\bar{c}$ = 1.000g/100ml, Δc = 2.000g/100ml

Temperature (°C)	Dexp	Dlit	Deviation (%)
25.0	5.19±0.05	5.148	+0.8
14.8	3.80±0.06	3.866	+1.7
2.6	2.54±0.02	2.53	+0.4

Table 3. Diffusion Coefficients ($m^2/s \times 10^9$) of Ethylene Glycol at 25.0°C

$\bar{c}^a$	Δc^a	$\bar{D}$exp	D^0exp	D^0lit	Deviation(%)
0.7507	1.5003	1.13±0.04			
10.2068	2.0331	1.02±0.01	1.14	1.16, 1.17	1.7
25.0109	1.9625	0.83±0.01			

a) wt%

Table 4. Concentration[a] of Essential Oil Components in Various Foods

Flavoring Substances	Beverages	Ice Cream	Candy	Baked Goods	Other
m-anisaldehyde	6.3	5.6	14.0	16.0	chewing gum-30
carvone	850	120	180	110	-
eugenol	1.4	3.1	32	33	chewing gum-500 meats-2,000
piperitone	11	18	-	-	-
pulegone	8.0	32	17	25	-

a) ppm(by volume)

Table 5. Regression Coefficients of Weightloss Curves

Solution	b	m	Correlation Coefficient
Sucrose(10%)	103.0	-6.2	-0.991
Glucose(10%)	100.7	-5.9	-1.000
Sodium Chloride(5%)	104.1	-5.8	-0.992
Gum Arabic(1%)	96.6	-5.0	-0.999

Table 6. Retention of Carvone, m-Anisaldehyde and Eugenol as a Function of Initial Glucose Content

Wt% Glucose	Retention (%)		
	Carvone[a]	m-Anisaldehyde[a]	Eugenol[a]
3	52 ±3.2	57.8±5.3	43.0±7.6
5	60.7±2.4	61.6±5.1	57.4±4.9
7	69.1±1.0	73.2±3.3	56.8±3.7
10	66.3±3.7	77.3±3.1	76.9±8.7
15	66.8±3.9	76.9±4.8	83.2±2.8

a) Initial volatile content, 500 ppm

Table 7. Retention of Carvone and m-Anisaldehyde as a Function of Initial Sodium Chloride Content

Wt% Sodium Chloride	Retention (%)	
	Carvone[a]	m-Anisaldehyde[b]
3	4.1±0.9	13.7±0.9
5	7.8±0.8	23.5±1.6
7.5	13.4±1.6	31.4±2.1
10	18.0±1.4	36.3±1.5

a) Initial carvone content, 300 ppm
b) Initial m-anisaldehyde content, 500 ppm

Table 8. Retention of Carvone and Piperitone as a Function of Freezing Rate

Volatile[a]	Solution	Volatile Retention (%)	
		Fast Freezing	Slow Freezing
carvone	10% sucrose	79.9±1.1	54.7±2.2
piperitone	10% sucrose	88.1±0.5	65.9±4.2
carvone	10% glucose	84.9±0.6	78.1±8.4
carvone	1% gum arabic	37.0±0.9	36.2±0.3
carvone	5% sodium chloride	10.8±0.8	12.9±1.2

a) Initial volatile content, 500 ppm

Table 9. Retention of Carvone, Eugenol and m-Anisaldehyde as a Function of Initial Ethanol Concentration in 10% Sucrose

Initial Ethanol Concentration	Volatile Retention(%)		
(ppm)	Carvone[a]	Eugenol[a]	m-Anisaldehyde[a]
0	53.0±1.3	58.3±1.4	56.8±1.1
300	54.4±2.8	59.3±2.4	56.2±2.2
600	53.9±2.2	61.7±1.2	58.3±0.6
900	52.5±4.6	58.9±2.4	57.6±1.3
1200	54.6±2.9	60.1±2.0	56.7±1.5

a) Initial volatile content, 500 ppm

Table 10. Retention of Carvone, Eugenol and m-Anisaldehyde as a Function of Initial Octanol Concentration in 10% Sucrose

Initial Octanol Concentration (ppm)	Volatile Retention (%)		
	Carvone[a]	Eugenol[a]	m-Anisaldehyde[a]
0	53.0±1.3	58.3±1.4	56.8±1.1
200	43.5±4.3	54.7±2.0	46.3±3.1
400	42.5±3.1	47.3±1.0	51.7±0.7
600	41.0±2.9	42.5±1.0	53.9±0.9
800	34.3±2.1	41.2±1.6	48.9±0.6

a) Initial volatile content, 500 ppm

Table 11. pH Values of 10% Sucrose Solutions at Various Stages of Sample Preparation and after Freeze Drying

Volatile[a]	pH 10% Sucrose Solution	pH After Volatile Added	pH of Rehydrated Freeze Dried Sample
carvone	2.9,5.5,7.0,8.5,10.3	3.0,4.8,7.0,7.4,10.1	not recorded
eugenol	2.9,5.5,7.0,8.5,10.3	2.9,5.5,6.6,7.3,9.8	2.8,6.0,7.1,7.6,8.1
piperitone	2.9,5.3,6.7,7.5,10.2	2.9,5.3,6.9,7.3,10.2	2.9,5.5,7.0,7.3,8.5
pulegone	2.9,5.3,6.7,7.5,10.2	2.9,4.8,6.1,6.9,10.0	2.9,5.5,6.7,7.1,8.4

a) Initial volatile content, 500 ppm

Table 12. Retention of Carvone in 5% Sodium Chloride as a Function of Initial pH

Initial pH	Volatile Retention (%)
	Carvone[a]
2.8	12.8±0.8
6.0	11.7±1.4
7.2	14.6±1.4
8.6	14.3±1.7
11.0	15.4±2.6

a) Initial volatile content, 500 ppm

Table 13. pH Values of 1% Gum Arabic Solutions at Various Stages of Solution Preparation and after Freeze Drying

Volatile[a]	pH before gum arabic added	pH after gum arabic added	pH after volatile added	pH of rehydrated samples
carvone	3.0,5.5,7.0,7.4,10.6	4.0,4.9,5.0,5.1,10.9	4.2,4.9,5.0,5.1,9.4	not recorded
eugenol	3.0,5.5,7.0,7.4,10.6	4.0,4.9,5.0,5.1,10.9	4.0,5.0,5.0,5.2,9.8	4.0,4.9,5.0,5.2,8.2
piperitone	2.8,5.0,7.0,8.0,11.0	3.9,4.9,5.0,5.2,10.7	3.9,4.9,5.0,5.5,9.6	4.0,5.0,5.2,5.3,8.3
pulegone	2.8,5.0,7.0,8.0,11.0	3.9,4.9,5.0,5.2,10.7	3.9,4.9,5.0,5.1,9.2	4.0,5.0,5.2,8.3

a) Initial volatile content, 500 ppm

Table 14. Absorbance of Rehydrated 10% Sucrose Samples at Low Initial Volatile Concentrations

Volatile	Initial volatile concentration (ppm)	Dilution factor prior to U.V.	Absorbance
Carvone	50	1:5	0.577
	25	2:5	0.621
	10	none	0.784
Piperitone	50	1:5	0.780
	25	2:5	0.822
	10	none	1.049

Table 15. Extinction Coefficients of Carvone, Pulegone and Piperitone in Water and Aqueous Solution

Solute	λmax(nm)	log ε	
		H_2O	EtOH
Carvone	241.5	3.92	3.93
Pulegone	263.0	3.80	3.91
Piperitone	242.5	4.03	4.11

Table 16. Solubilities of Piperitone in Aqueous Solutions of Sucrose, Glucose and Sodium Chloride at 10, 20 and 30°C

Dissolved Solid	wt%	Solubility (g/l) 10°C	20°C	30°C
Sucrose	0	3.00	2.52	2.36
	10	2.82	2.40	2.34
	20	2.60	2.24	2.10
	30	2.34	2.07	1.96
	40	2.05	1.87	1.81
	50	1.71	1.65	1.64
Glucose	0	2.99	2.56	2.35
	8	2.33	2.27	2.17
	16	2.09	2.00	1.94
	24	1.87	1.74	1.70
	32	1.55	1.50	1.46
	40	1.30	1.28	1.26
Sodium Chloride	0	3.02	2.52	2.37
	4	1.99	1.67	1.57
	8	1.31	1.11	1.03
	12	0.88	0.76	0.68
	16	0.58	0.51	0.44
	20	0.31	0.27	0.23

Table 17. Solubilities of Pulegone in Aqueous Solutions of Sucrose, Glucose and Sodium Chloride at 10, 20 and 30°C

Dissolved Solid	wt%	Solubility (g/l) 10°C	20°C	30°C
Sucrose	0	1.62	1.38	1.22
	10	1.49	1.29	1.15
	20	1.36	1.19	1.04
	30	1.21	1.08	0.92
	40	1.04	0.97	0.82
	50	0.87	0.85	0.77
Glucose	0	1.60	1.37	1.26
	8	1.38	1.24	1.13
	16	1.17	1.10	1.01
	24	0.99	0.94	0.88
	32	0.82	0.79	0.76
	40	0.66	0.66	0.63
Sodium Chloride	0	1.62	1.38	1.28
	4	1.06	0.87	0.82
	8	0.68	0.55	0.52
	12	0.43	0.37	0.33
	16	0.27	0.25	0.21
	20	0.14	0.13	0.13

Table 18. Solubilities of Carvone in Aqueous Solutions of Sucrose, Glucose and Sodium Chloride at 10, 20 and 30°C

Dissolved Solid	wt%	Solubility (g/l) 10°C	20°C	30°C
Sucrose	0	1.66	1.50	1.60
	10	1.57	1.47	1.54
	20	1.46	1.40	1.47
	30	1.34	1.31	1.38
	40	1.20	1.22	1.29
	50	1.05	1.12	1.18
Glucose	0	1.70	1.55	1.62
	10	1.40	1.38	1.42
	20	1.19	1.21	1.27
	30	0.99	1.04	1.15
	40	0.78	0.87	1.04
	50	0.63	0.70	0.93
Sodium Chloride	0	1.73	1.57	1.61
	4	1.18	1.10	1.15
	8	0.80	0.73	0.77
	12	0.54	0.50	0.49
	16	0.36	0.38	0.29
	20	0.21	0.20	0.18

Table 19. Activity Coefficients of Piperitone in Saturated Aqueous Solutions at 10, 20 and 30°C

Dissolved Solid	wt%	Activity Coefficients		
		10°C	20°C	30°C
Sucrose	0	2811	3341	3559
	10	2815	3312	3537
	20	2846	3296	3508
	30	2911	3292	3467
	40	3021	3297	3405
	50	3204	3313	3312
Glucose	0	2818	3280	3571
	8	3472	3547	3703
	16	3677	3845	3941
	24	3885	4179	4272
	32	4405	4551	4660
	40	4887	4966	5010
Sodium Chloride	0	2797	3339	3551
	4	4300	5114	5434
	8	6599	7760	8369
	12	9977	11515	12817
	16	15263	17319	20112
	20	28778	33033	39239

Table 20. Activity Coefficients of Pulegone in Saturated Aqueous Solutions at 10, 20 and 30°C

Dissolved Solid	wt%	Activity Coefficient		
		10°C	20°C	30°C
Sucrose	0	5225	6110	6924
	10	5328	6148	6861
	20	5472	6227	7107
	30	5667	6310	7434
	40	5935	6373	7545
	50	6322	6408	7104
Glucose	0	5264	6165	6696
	8	5860	6496	7119
	16	6562	7016	7623
	24	7393	7735	8239
	32	8384	8632	9017
	40	9569	9598	10049
Sodium Chloride	0	5211	6114	6589
	4	8047	9869	10378
	8	12688	15648	16651
	12	20259	23562	26551
	16	33211	34924	41651
	20	64524	68829	69840

Table 21. Activity Coefficients of Carvone in Saturated Aqueous Solutions at 10, 20 and 30°C

Dissolved Solid	wt%	Activity Coefficient 10°C	20°C	30°C
Sucrose	0	5013	5563	5196
	10	5004	5322	5069
	20	5013	5223	4953
	30	5039	5126	4839
	40	5082	4979	4720
	50	5143	4827	4582
Glucose	0	4910	5385	5138
	10	5618	5723	5533
	20	6210	6124	5805
	30	6961	6613	5950
	40	8055	7231	6000
	50	8974	8068	6020
Sodium Chloride	0	4806	5286	5157
	4	7169	7659	7330
	8	10731	11744	11025
	12	15996	17163	17697
	16	24233	23003	30079
	20	42627	43325	48533

Table 22. Partial Molar Heats of Hydration, ΔH_h, and Partial Molar Heats of Solution, ΔH_s, for Piperitone Saturated Aqueous Solutions

Dissolved Solid	wt%	Temperature (°C)					
		10		20		30	
		$-\Delta H_h$ Jmole^{-1}	$-\Delta H_s$ Jmole^{-1}	$-\Delta H_h$ Jmole^{-1}	$-\Delta H_s$ Jmole^{-1}	$-\Delta H_h$ Jmole^{-1}	$-\Delta H_s$ Jmole^{-1}
Sucrose	0	76731	16051	68145	-7991	61169	-1548
	10	75534	14854	67923	-7769	61726	-2105
	20	73956	13276	67287	-7133	61843	-2222
	30	71823	11143	66114	5960	61438	-1817
	40	68808	8128	64206	4052	60415	794
	50	64306	3626	61199	1045	58602	-1018
Glucose	0	73555	12875	68355	8200	64084	4464
	8	61183	503	62557	2403	63543	3922
	16	64482	3802	62551	2397	60895	1274
	24	67642	6963	63336	3182	59780	159
	32	63229	2549	62134	1980	61146	1525
	40	62035	1354	61017	863	60090	470
Sodium Chloride	0	77278	16598	68207	8053	60843	1222
	4	76920	16240	68059	7905	60863	1242
	8	75065	14385	68294	8140	62769	3148
	12	71710	11030	68974	8820	66675	7055
	16	68073	7393	70138	9983	71674	12054
	20	68366	7686	71411	11257	73732	14111

Table 23. Partial Molar Free Energies of Hydration, ΔGh, and Partial Molar Free Energies of Solution, ΔGs, for Piperitone Saturated Aqueous Solutions

Dissolved Solid	wt%	Temperature (°C)					
		10		20		30	
		ΔGh $Jmole^{-1}$	ΔGs $Jmole^{-1}$	ΔGh $Jmole^{-1}$	ΔGs $Jmole^{-1}$	ΔGh $Jmole^{-1}$	ΔGs $Jmole^{-1}$
Sucrose	0	23228	18695	26285	19776	29096	20611
	10	23231	18699	26264	19755	29080	20595
	20	23257	18725	26252	19744	29059	20574
	30	23310	18777	26249	19740	29029	20544
	40	23398	18865	26253	19745	28984	20499
	50	23536	19003	26265	19756	28914	20429
Glucose	0	23234	18701	26240	19731	29104	20619
	8	23725	19192	26431	19922	29195	20710
	16	23860	19328	26628	20119	29353	20868
	24	23990	19457	26831	20322	29556	21071
	32	24286	19753	27039	20530	29775	21290
	40	24530	19997	27251	20742	20058	21473
Sodium Chloride	0	23217	18684	26284	19775	29090	20605
	4	24229	19696	27323	20814	30162	21677
	8	25237	20704	28339	21831	31251	22766
	12	26210	21677	29301	22793	32325	23840
	16	27211	22678	30296	23787	33461	24976
	20	28704	24171	31870	25361	35145	26660

Table 24. Partial Molar Entropies of Hydration, ΔSh, and Partial Molar Entropies of Solution, ΔSs, for Piperitone Saturated Aqueous Solutions

Dissolved Solid	wt%	Temperature (°C) 10		20		30	
		$-\Delta Sh$ $Jmole^{-1}°K^{-1}$	$-\Delta Ss$ $Jmole^{-1}°K^{-1}$	$-\Delta Sh$ $Jmole^{-1}°K^{-1}$	$-\Delta Ss$ $Jmole^{-1}°K^{-1}$	$-\Delta Sh$ $Jmole^{-1}°K^{-1}$	$-\Delta Ss$ $Jmole^{-1}°K^{-1}$
Sucrose	0	353	123	322	95	298	73
	10	349	119	321	94	300	75
	20	343	113	319	92	300	75
	30	336	106	315	88	298	74
	40	326	95	309	81	295	70
	50	310	80	298	71	289	64
Glucose	0	342	112	323	95	307	83
	8	300	70	304	76	306	81
	16	312	82	304	77	298	73
	24	324	93	308	80	295	70
	32	309	79	304	77	300	75
	40	306	75	301	74	297	72
Sodium Chloride	0	355	125	322	95	297	72
	4	357	127	325	98	300	76
	8	354	124	330	102	310	86
	12	346	116	335	108	327	102
	16	337	106	343	115	347	122
	20	343	113	353	125	359	135

Table 25. Partial Molar Enthalpies of Hydration, ΔHh, and Partial Molar Enthalpies of Solution, ΔHs, for Pulegone Saturated Aqueous Solutions.

Dissolved Solid	wt%	Temperature (°C)					
		10		20		30	
		$-\Delta Hh$ Jmole^{-1}	$-\Delta Hs$ Jmole^{-1}	$-\Delta Hh$ Jmole^{-1}	$-\Delta Hs$ Jmole^{-1}	$-\Delta Hh$ Jmole^{-1}	$-\Delta Hs$ Jmole^{-1}
Sucrose	0	71113	11702	68836	9954	66901	8557
	10	70294	10883	67801	8919	65693	7349
	20	67850	8439	68266	9385	68484	10141
	30	64167	4756	68851	9969	72480	14137
	40	60010	598	67903	9022	74099	15755
	50	56531	-2881	63445	4564	68858	10514
Glucose	0	73052	13641	67178	8296	62368	4024
	8	66709	7297	65808	6927	64974	6631
	16	63159	3748	64323	5441	65139	6795
	24	61644	2232	62840	3958	63682	5338
	32	60729	1317	61550	2668	62091	3748
	40	57796	1615	60820	1939	63123	4780
Sodium Chloride	0	73597	14185	66923	8042	61474	3131
	4	79401	19989	67337	8455	57580	-764
	8	79518	20107	67991	9109	58662	319
	12	70750	11338	68437	9555	66474	8130
	16	57437	-1975	67534	8652	75491	17147
	20	65797	-6385	61504	2622	57958	386

Table 26. Partial Molar Free Energies, ΔGh, and Partial Molar Free Energies of Solution, ΔGs, for Pulegone Saturated Aqueous Solutions

Dissolved Solid	wt%	Temperature (°C)					
		10		20		30	
		ΔGh $Jmole^{-1}$	ΔGs $Jmole^{-1}$	ΔGh $Jmole^{-1}$	ΔGs $Jmole^{-1}$	ΔGh $Jmole^{-1}$	ΔGs $Jmole^{-1}$
Sucrose	0	20795	20155	24681	21248	28445	22288
	10	20841	20201	24696	21263	28422	22265
	20	20904	20263	24727	21294	28511	22354
	30	20986	20346	24759	21327	28625	22467
	40	21095	20455	24783	21351	28662	22505
	50	21244	20603	24797	21364	28510	22353
Glucose	0	20813	20172	24703	21270	28361	22203
	8	19146	20425	24830	21397	28516	22358
	16	19481	20691	25018	21584	28688	22530
	24	19784	20972	25255	21823	28884	22726
	32	20089	21268	25523	22090	29111	22954
	40	20458	21579	25781	22349	29384	23227
Sodium Chloride	0	20789	20148	24682	21250	28320	22163
	4	21812	21172	25849	22416	29466	23308
	8	22884	21434	26973	23540	30657	24500
	12	23985	22718	27970	24538	31833	25676
	16	25149	24160	28930	25497	32968	26810
	20	26712	25475	30583	27150	34271	28113

Table 27. Partial Molar Entropies of Hydration, ΔSh, and Partial Molar Entropies of Solution, ΔSs, for Pulegone Saturated Aqueous Solutions

Dissolved Solid	wt%	Temperature (°C) 10		20		30	
		$-\Delta Sh$ $Jmole^{-1}°K^{-1}$	$-\Delta Ss$ $Jmole^{-1}°K^{-1}$	$-\Delta Sh$ $Jmole^{-1}°K^{-1}$	$-\Delta Ss$ $Jmole^{-1}°K^{-1}$	$-\Delta Sh$ $Jmole^{-1}°K^{-1}$	$-\Delta Ss$ $Jmole^{-1}°K^{-1}$
Sucrose	0	325	113	319	106	315	102
	10	322	110	316	103	310	98
	20	313	101	317	105	320	107
	30	301	89	319	107	334	121
	40	286	74	316	104	339	126
	50	275	63	301	88	321	108
Glucose	0	332	119	313	101	299	87
	8	310	98	309	97	308	96
	16	298	86	305	92	310	97
	24	294	82	301	88	305	93
	32	292	80	297	85	301	88
	40	283	71	295	83	305	92
Sodium Chloride	0	333	121	313	100	296	83
	4	357	145	318	105	287	74
	8	362	150	324	111	295	82
	12	335	123	329	116	324	112
	16	292	80	329	117	358	145
	20	327	115	314	102	304	92

Table 28. Partial Molar Enthalpies of Hydration, ΔHh, and Partial Molar Enthalpies of Solution, ΔHs, for Carvone Saturated Aqueous Solutions

Dissolved Solid	wt%	Temperature (°C)					
		10		20		30	
		$-\Delta Hh$ Jmole^{-1}	$-\Delta Hs$ Jmole^{-1}	$-\Delta Hh$ Jmole^{-1}	$-\Delta Hs$ Jmole^{-1}	$-\Delta Hh$ Jmole^{-1}	$-\Delta Hs$ Jmole^{-1}
Sucrose	0	74637	14155	60501	543	49090	-10338
	10	69227	8745	59949	-9	52420	-7007
	20	67163	6681	59123	-835	52584	-6843
	30	64759	4277	58190	-1768	52827	-6601
	40	60530	48	57171	-2787	54373	-5054
	50	55815	4667	55867	-4091	55797	-3631
Glucose	0	72460	11978	60983	1025	51697	-7731
	10	63910	3429	59191	-768	55306	-4122
	20	61226	744	57372	-2587	54178	-5249
	30	59369	-1113	54103	-5856	49781	-9647
	40	56654	-3828	49070	-10888	42896	-16531
	50	61297	815	44853	-15105	31397	-27831
Sodium Chloride	0	71830	11348	61947	2016	53984	-5444
	4	69500	9019	60285	327	52806	-6621
	8	72930	12448	60270	311	50037	-9391
	12	66826	6344	63410	3451	60566	1138
	16	43531	-16951	69074	9115	89379	29952
	20	57456	3026	65024	5066	70961	11534

Table 29. Partial Molar Free Energies of Hydration, ΔGh, and Partial Molar Free Energies of Solution, ΔGs, for Carvone Saturated Aqueous Solutions

Dissolved Solid	wt%	Temperature (°C)					
		10		20		30	
		ΔGh $Jmole^{-1}$	ΔGs $Jmole^{-1}$	ΔGh $Jmole^{-1}$	ΔGs $Jmole^{-1}$	ΔGh $Jmole^{-1}$	ΔGs $Jmole^{-1}$
Sucrose	0	23516	20057	26601	21019	29260	21564
	10	23511	20052	26493	20911	29198	21502
	20	23516	20057	26447	20865	29139	21444
	30	23528	20069	26401	20820	29081	21385
	40	23548	20089	26331	20749	29018	21322
	50	23576	20117	26255	20673	28943	21247
Glucose	0	23467	20009	26512	20940	29231	21536
	10	23784	20325	26670	21088	29418	21723
	20	24020	20561	26835	21254	29539	21844
	30	24288	20830	27022	21441	29601	21906
	40	24632	21174	27240	21658	29623	21927
	50	24886	21428	27507	21925	29631	21935
Sodium Chloride	0	23416	19958	26476	20895	29241	21545
	4	24358	20899	27380	21799	30127	22432
	8	25307	21849	28422	22841	31156	23460
	12	26247	22789	29347	23765	32349	24653
	16	27255	23767	30061	24479	33686	25990
	20	28555	25096	31604	26022	34891	27196

Table 30. Partial Molar Entropies of Hydration, ΔSh, and Partial Molar Entropies of Solution, ΔSs, for Carvone Saturated Aqueous Solutions

Dissolved Solid	wt%	Temperature (°C) 10		20		30	
		$-\Delta Sh$ Jmole^{-1}°K^{-1}	$-\Delta Ss$ Jmole^{-1}°K^{-1}	$-\Delta Sh$ Jmole^{-1}°K^{-1}	$-\Delta Ss$ Jmole^{-1}°K^{-1}	$-\Delta Sh$ Jmole^{-1}°K^{-1}	$-\Delta Ss$ Jmole^{-1}°K^{-1}
Sucrose	0	397	121	297	74	258	37
	10	328	102	295	71	269	48
	20	320	94	292	68	270	48
	30	312	86	289	65	270	49
	40	297	71	285	61	275	54
	50	280	55	280	57	280	58
Glucose	0	339	113	299	75	267	46
	10	310	84	293	69	280	58
	20	301	75	287	64	276	55
	30	295	70	277	53	262	40
	40	287	61	260	37	239	18
	50	304	79	247	23	202	-19.4
Sodium Chloride	0	336	111	302	78	275	53
	4	332	106	299	76	274	52
	8	347	121	303	79	268	46
	12	329	103	316	93	307	85
	16	250	24	338	115	410	185
	20	304	78	329	106	350	128

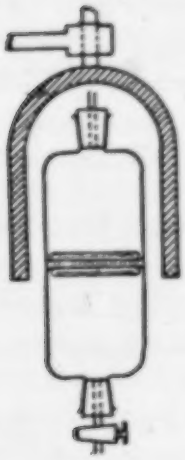


Figure 1. The Stokes diaphragm cell.

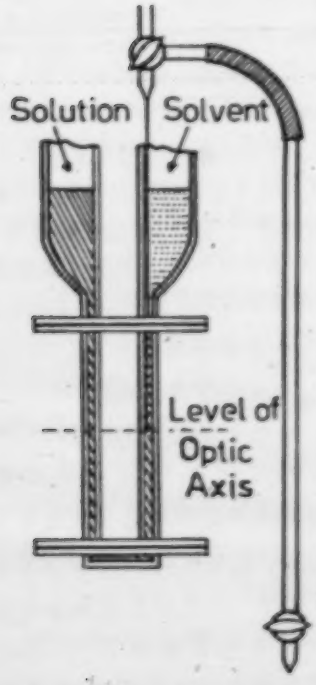


Figure 2. The Kahn and Polson boundary sharpening technique as applied to a Tiselius electrophoresis cell used for diffusion measurements.

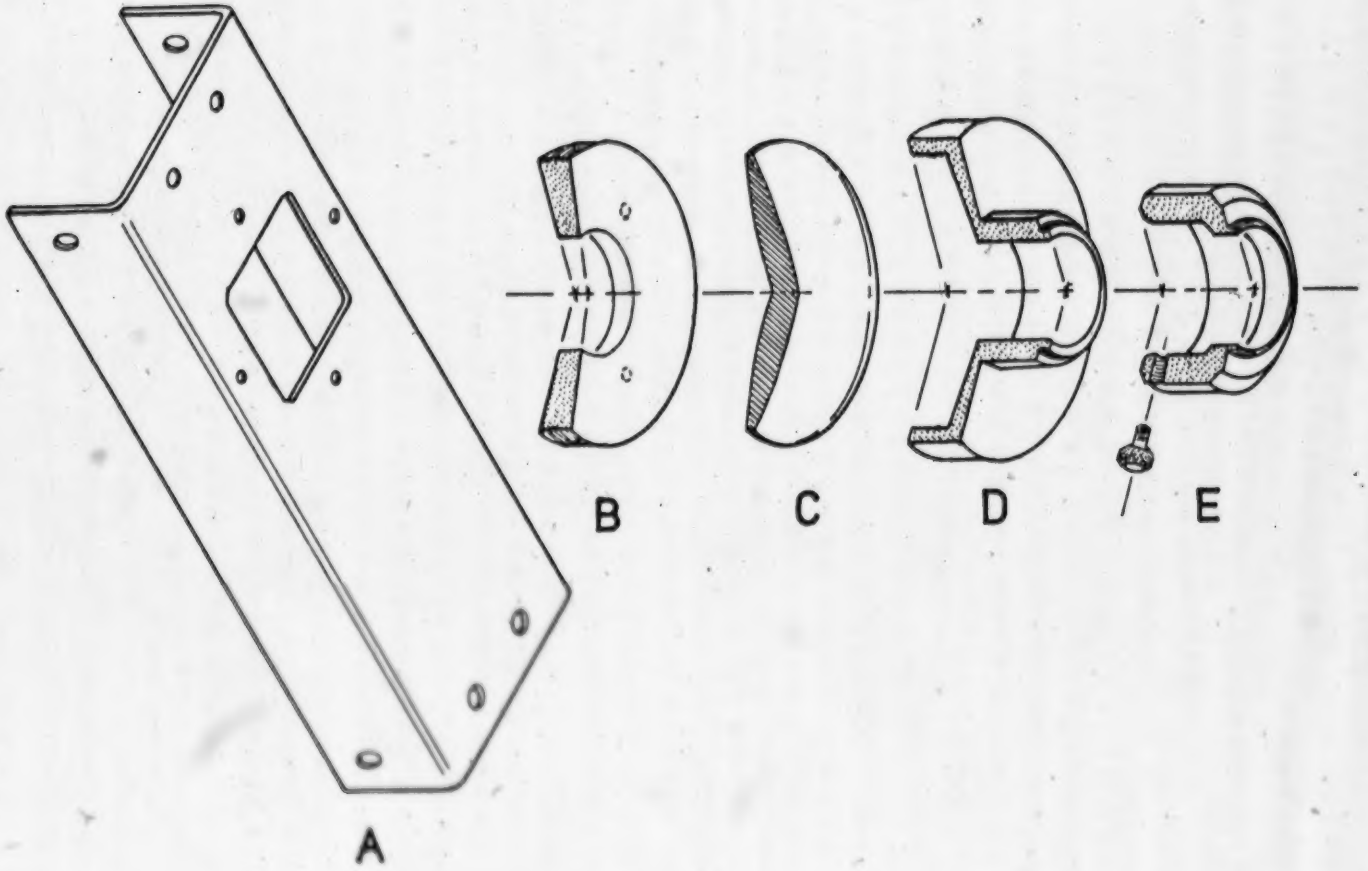


Figure 3. Adaptation of the 35 mm camera to the optical column of the schlieren accessory.

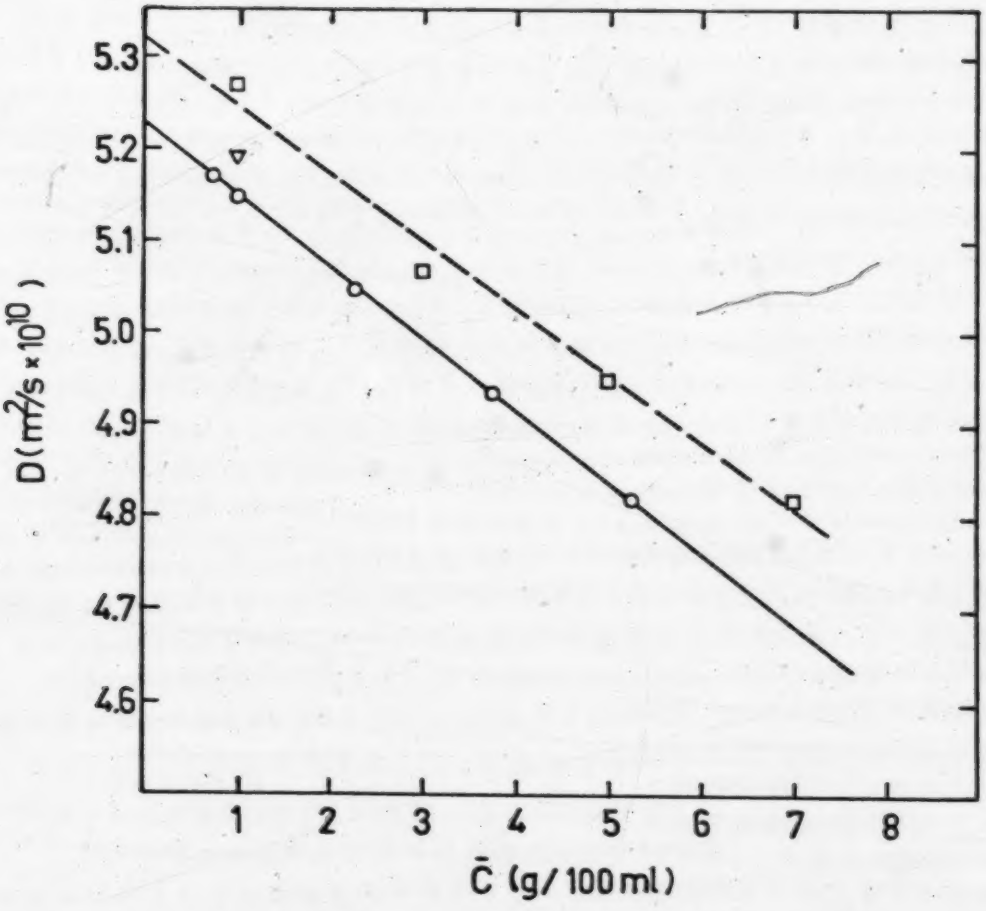


Figure 4. D as a function of the average sucrose concentration. □ , this work at 25.3°C; O, Gosting and Morris (1949) at 24.95°C; ▽, this work at 25.0°C; ____, best fit of data at 25.3°C.

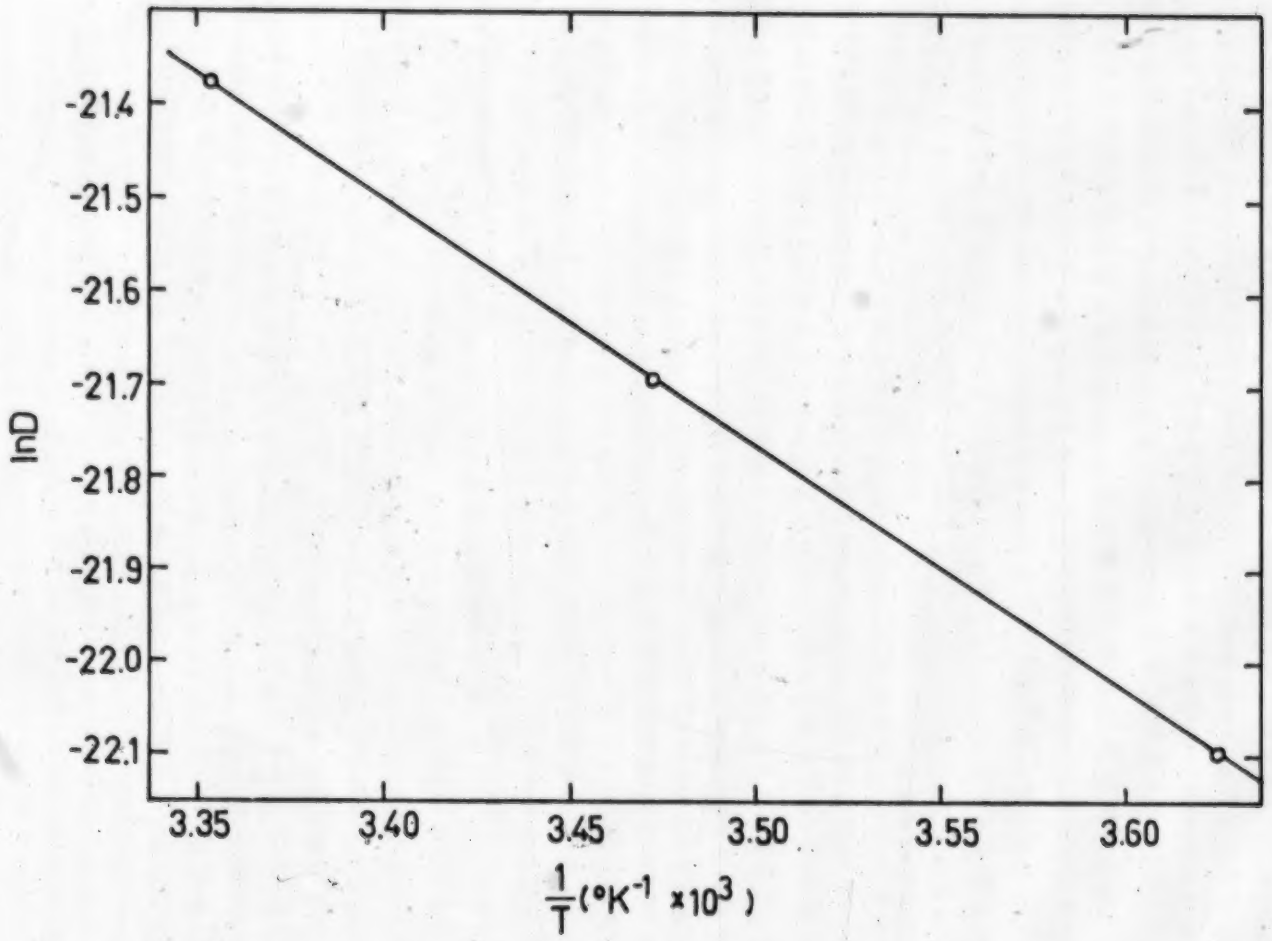


Figure 5. Arrhenius type plot of D and T.

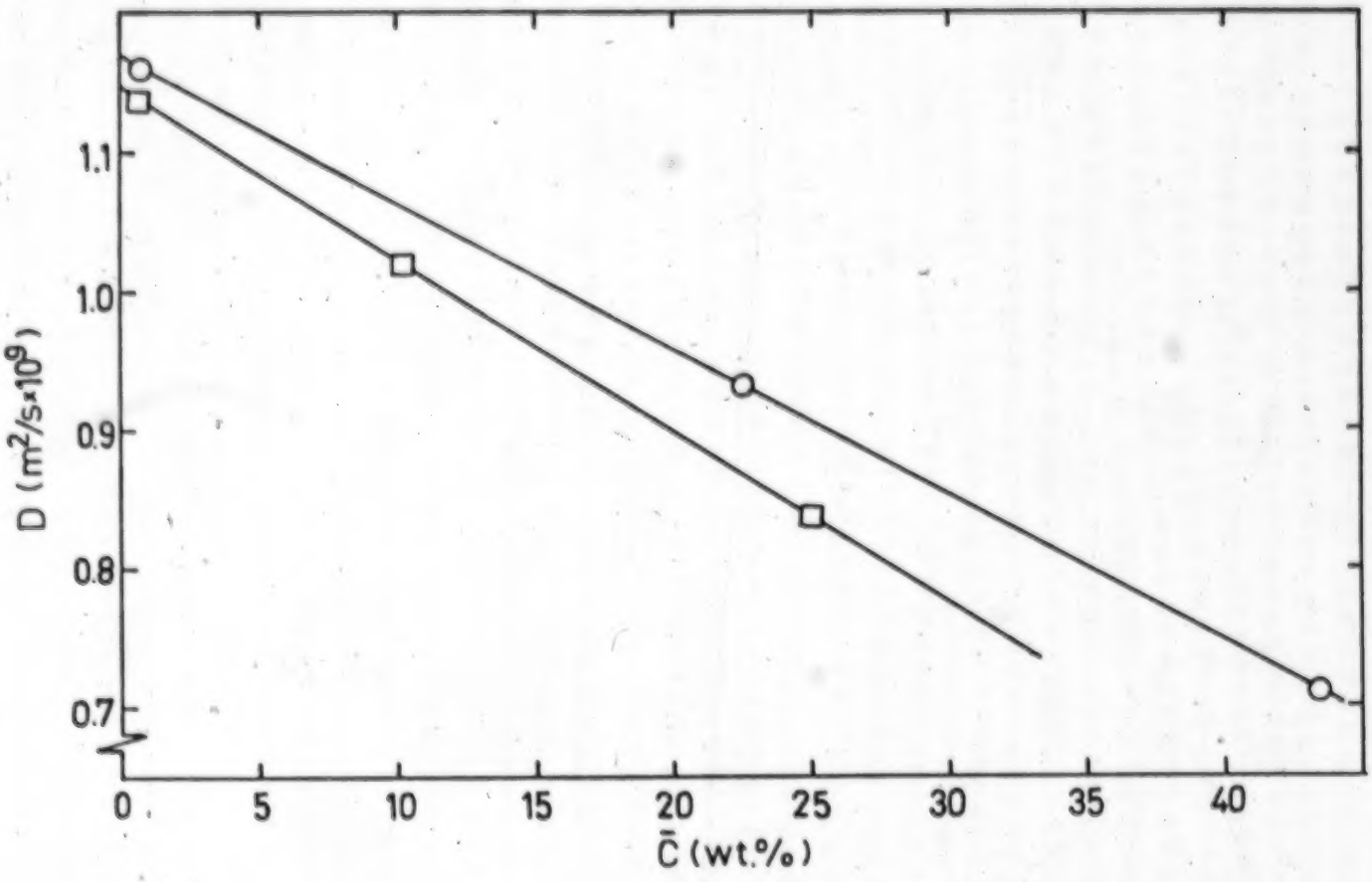


Figure 6. D as a function of average ethylene glycol concentration. □, this work; O, Byers and King (1966).

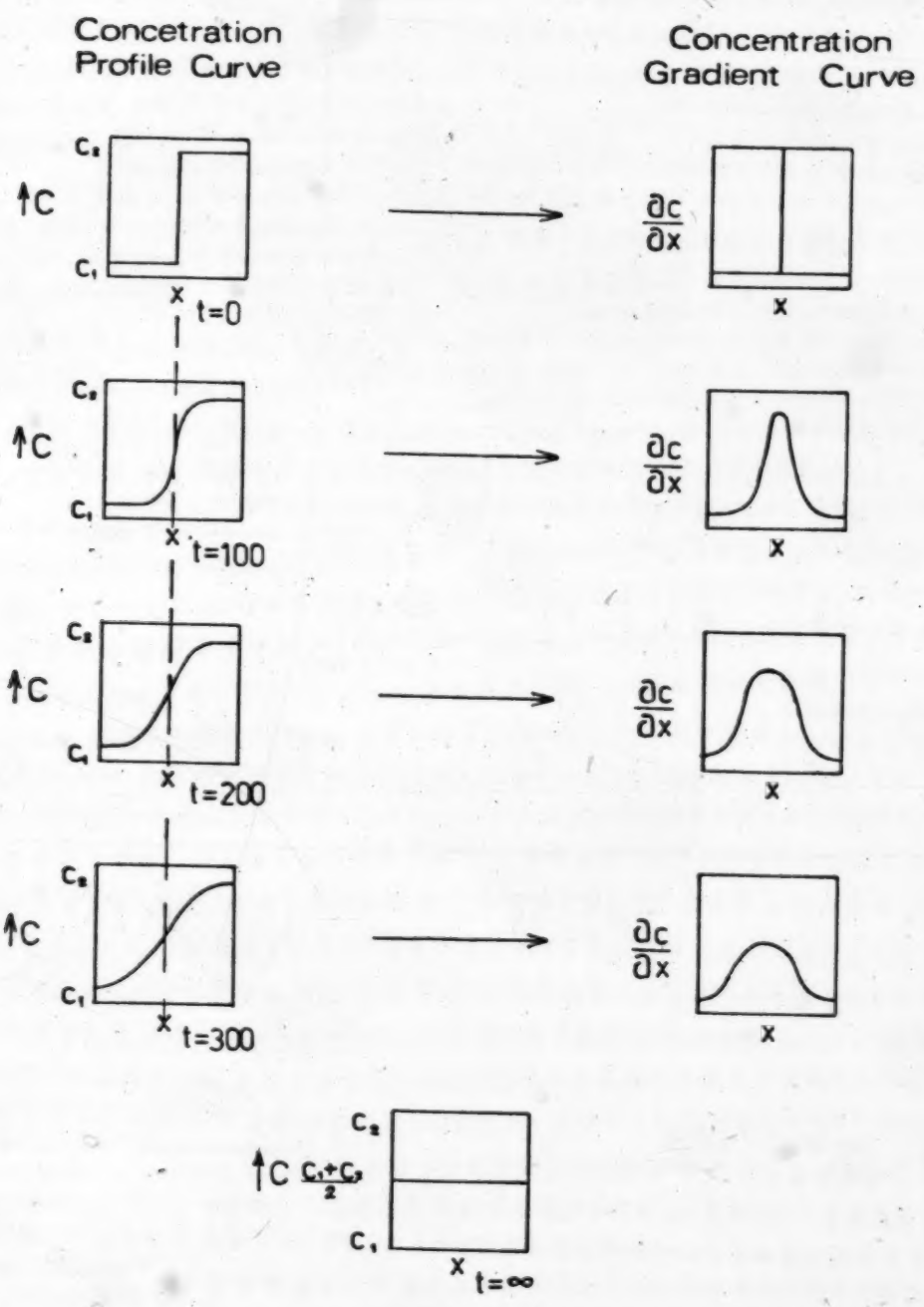
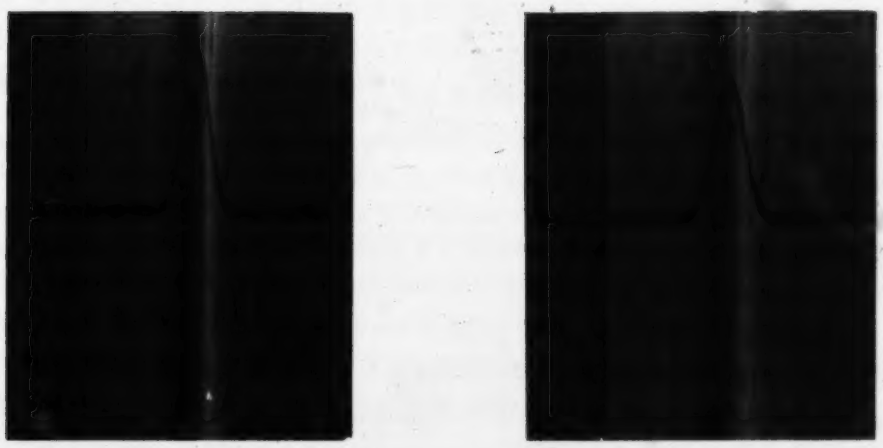
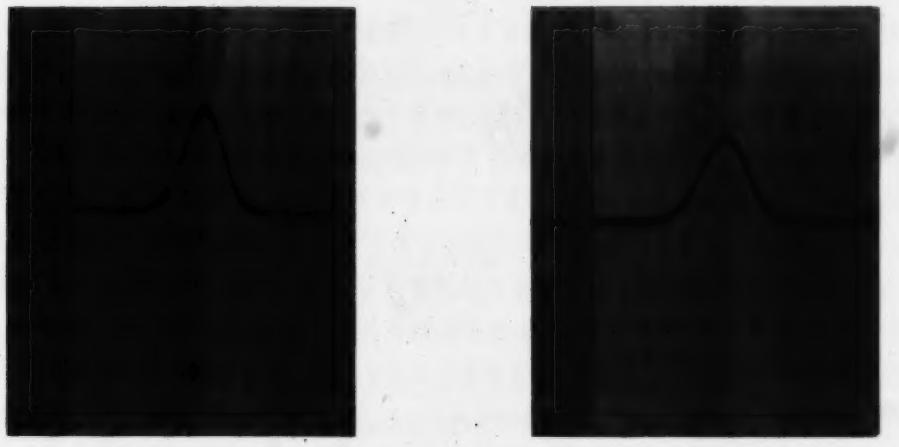


Figure 7. Theoretical diffusion experiment showing concentration curves and concentration gradient curves as a function of time.



θ = 180s

θ = 240s



θ = 300s

θ = 360s

Figure 8. Decrease of the photographically recorded schlieren image and time.

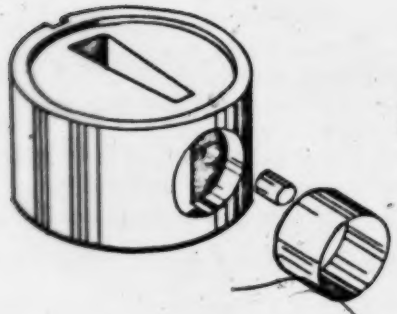
a. $\theta = 75°$

b. $\theta = 80°$

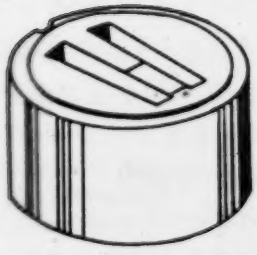
c. $\theta = 60°$

d. $\theta = 50°$

Figure 9. Influence of the schlieren bar angle on the photographic images.

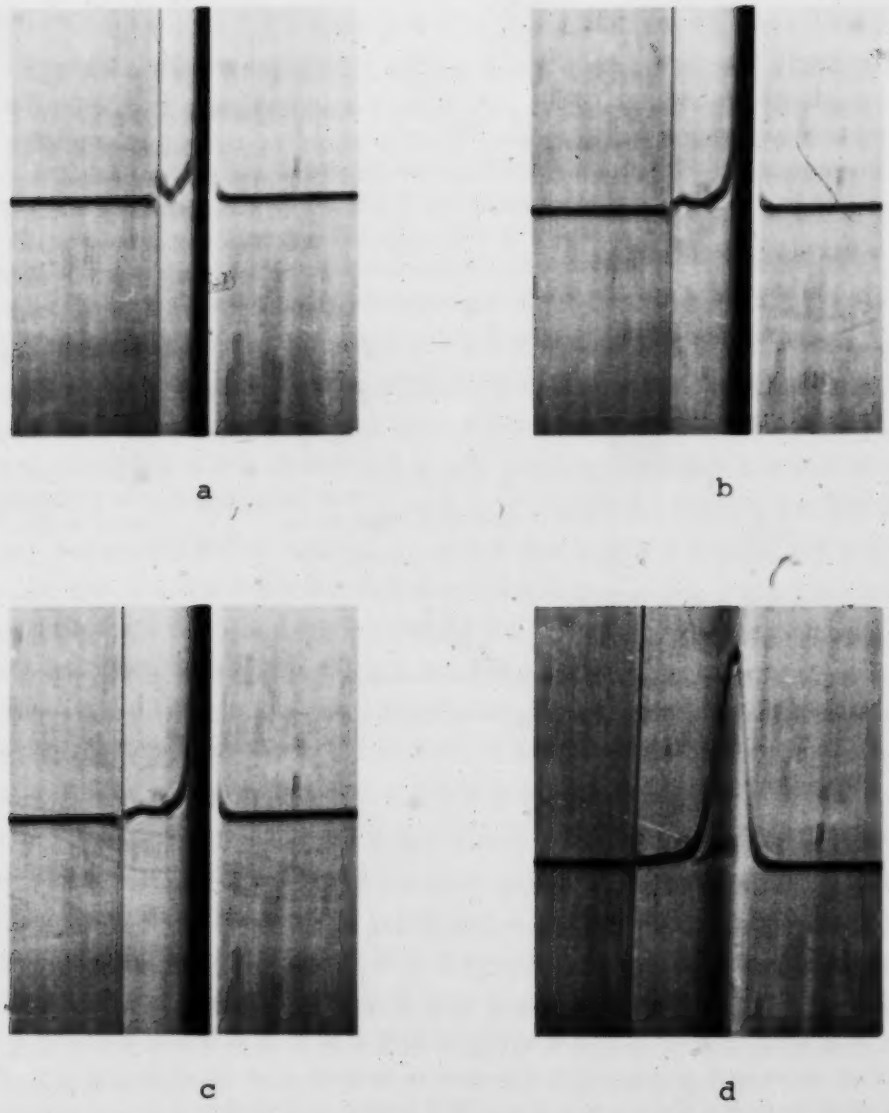


Valve-type synthetic boundary cell



Double-sector capillary synthetic boundary cell

Figure 10. Centerpieces for achieving boundary formation in an ultracentrifuge.



a b

c d

Figure 11. Boundary formation in the valve-type synthetic boundary cell as monitored photographically.

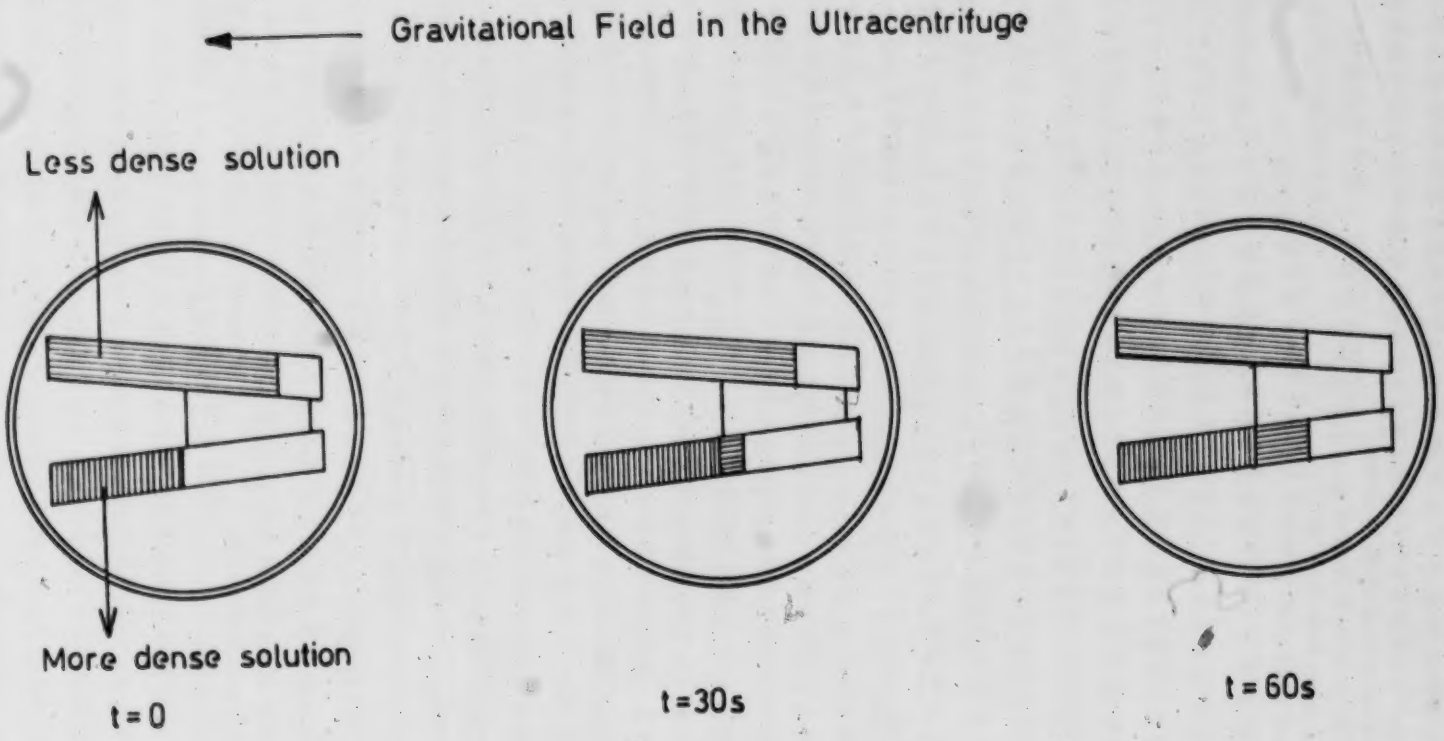
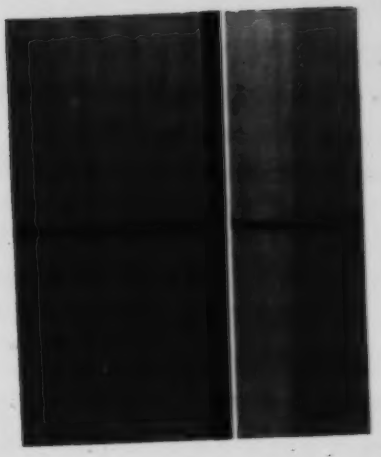


Figure 12. Mechanism of boundary formation in the double sector capillary synthetic boundary cell.

a. θ = 15s



b. θ = 30s

c. θ = 45s

d. θ = 60s

Figure 13. Boundary formation in the double sector capillary synthetic boundary cell as monitored photographically.

e. θ = 75s

f. θ = 90s

g. θ = 105s

h. θ = 180s

Figure 13 (cont'd). Boundary formation in the double sector capillary synthetic boundary cell as monitored photographically.

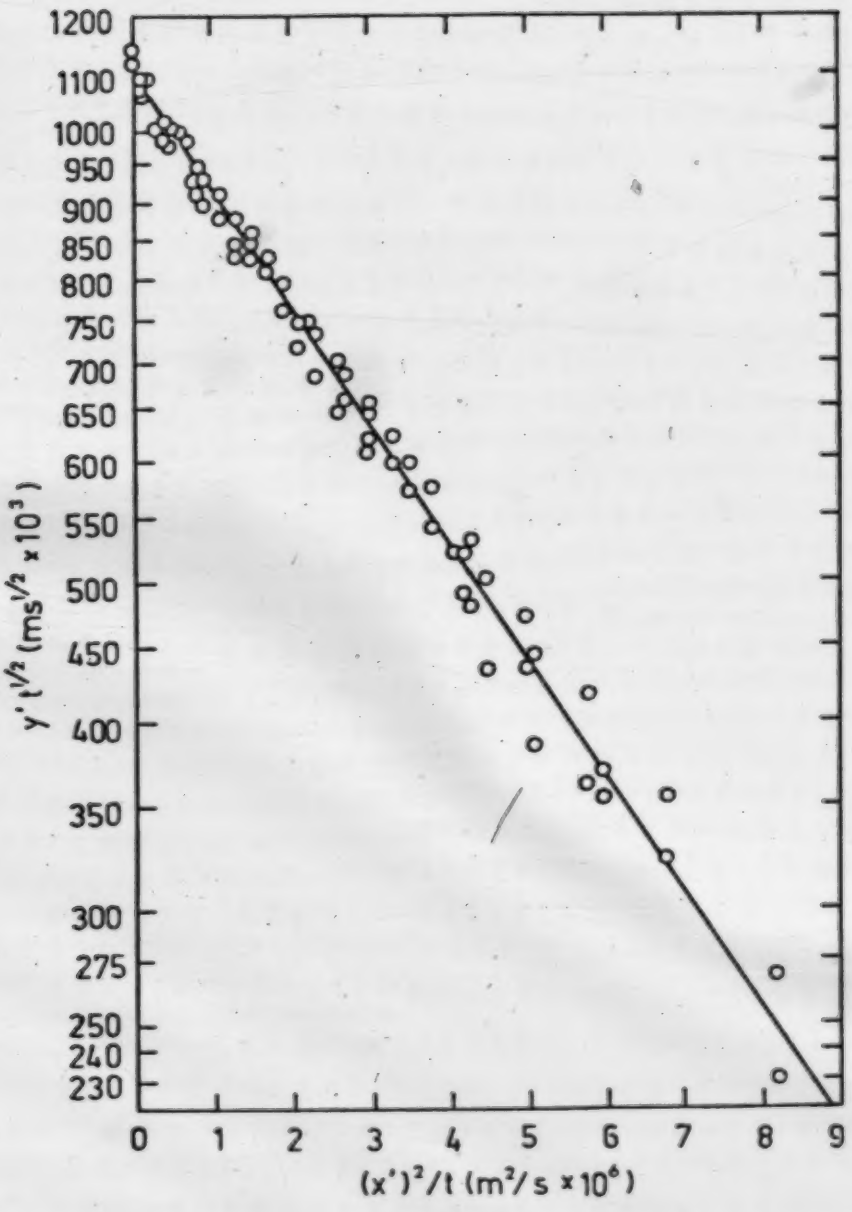


Figure 14. Plot of Equation 5 for glycine at 25.0°C.

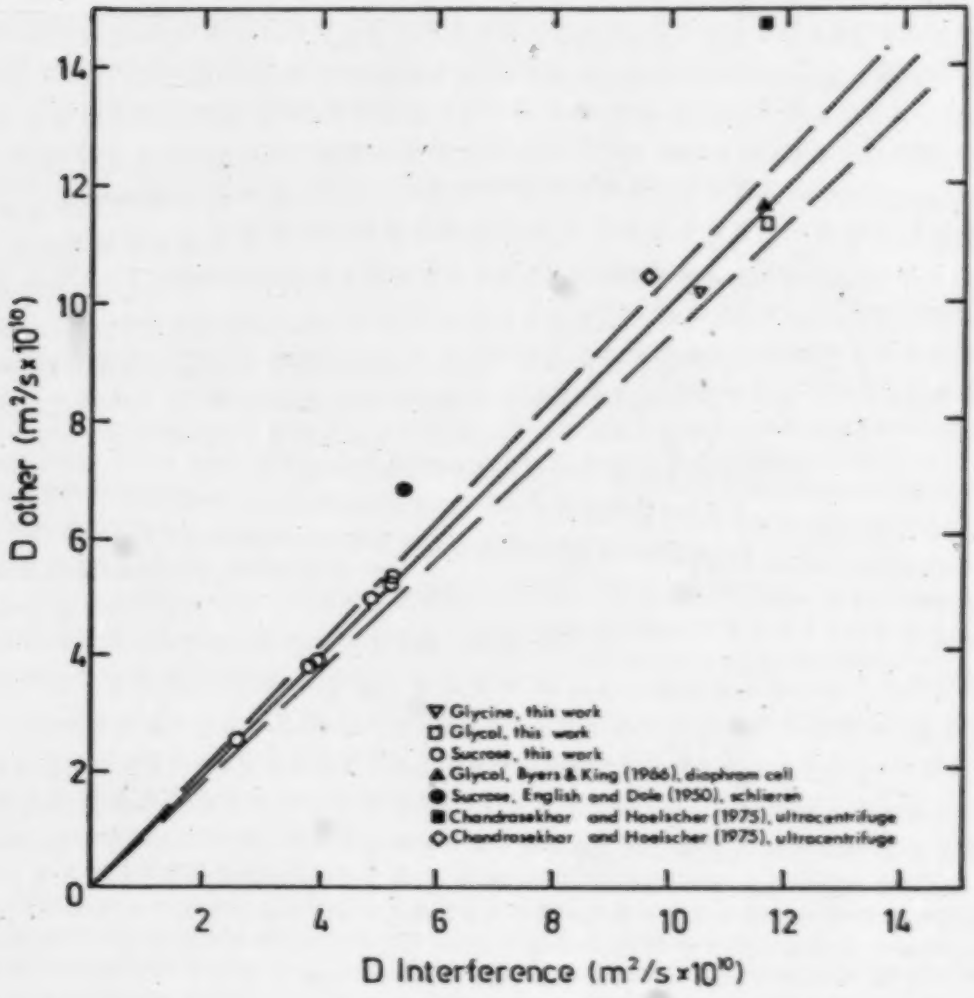


Figure 15. Dinterference vs. Dother.

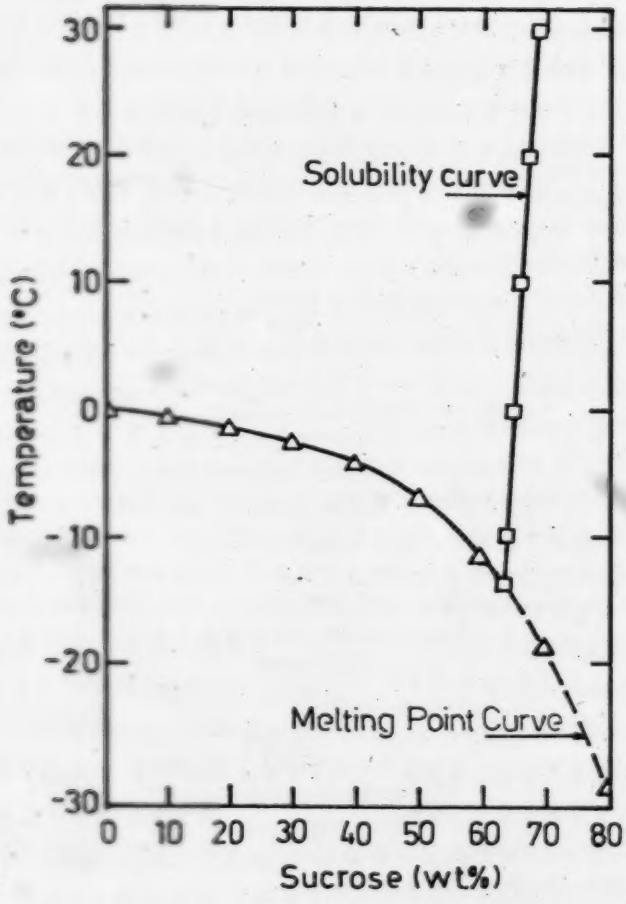


Figure 16. Sucrose-water phase diagram.

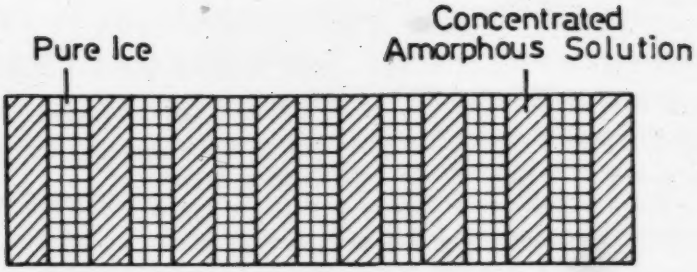


Figure 17. Cross section of a frozen solution.

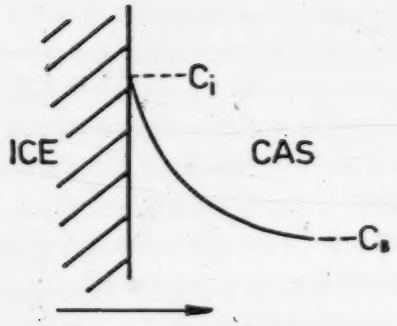


Figure 18. Concentration polarization effect of dissolved solids in the CAS during freezing (C_i, interface concentration; C_b, bulk concentration).

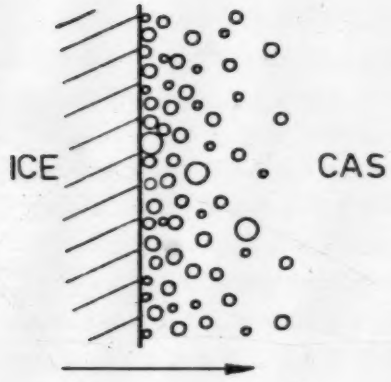


Figure 19. Concentration polarization of volatile above the solubility limit during freezing.

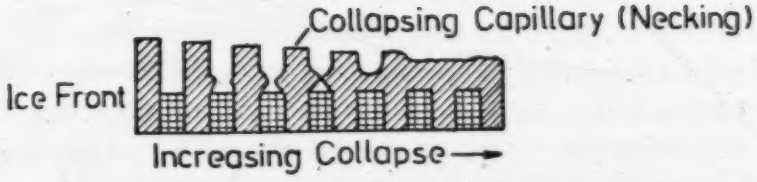


Figure 20. Progressive stages of collapse.

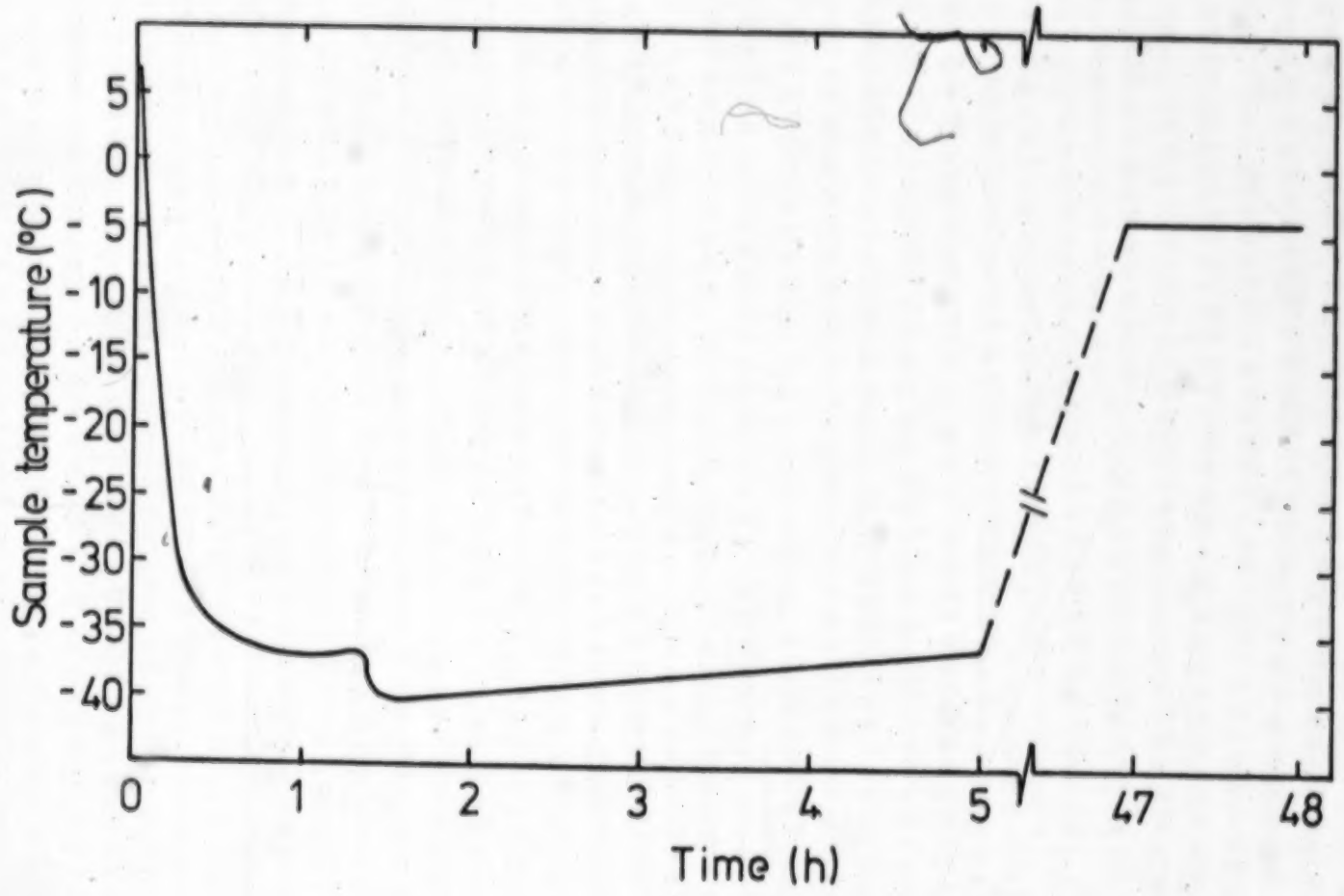


Figure 21. Temperature history of 20% sucrose sample during freezing and drying.

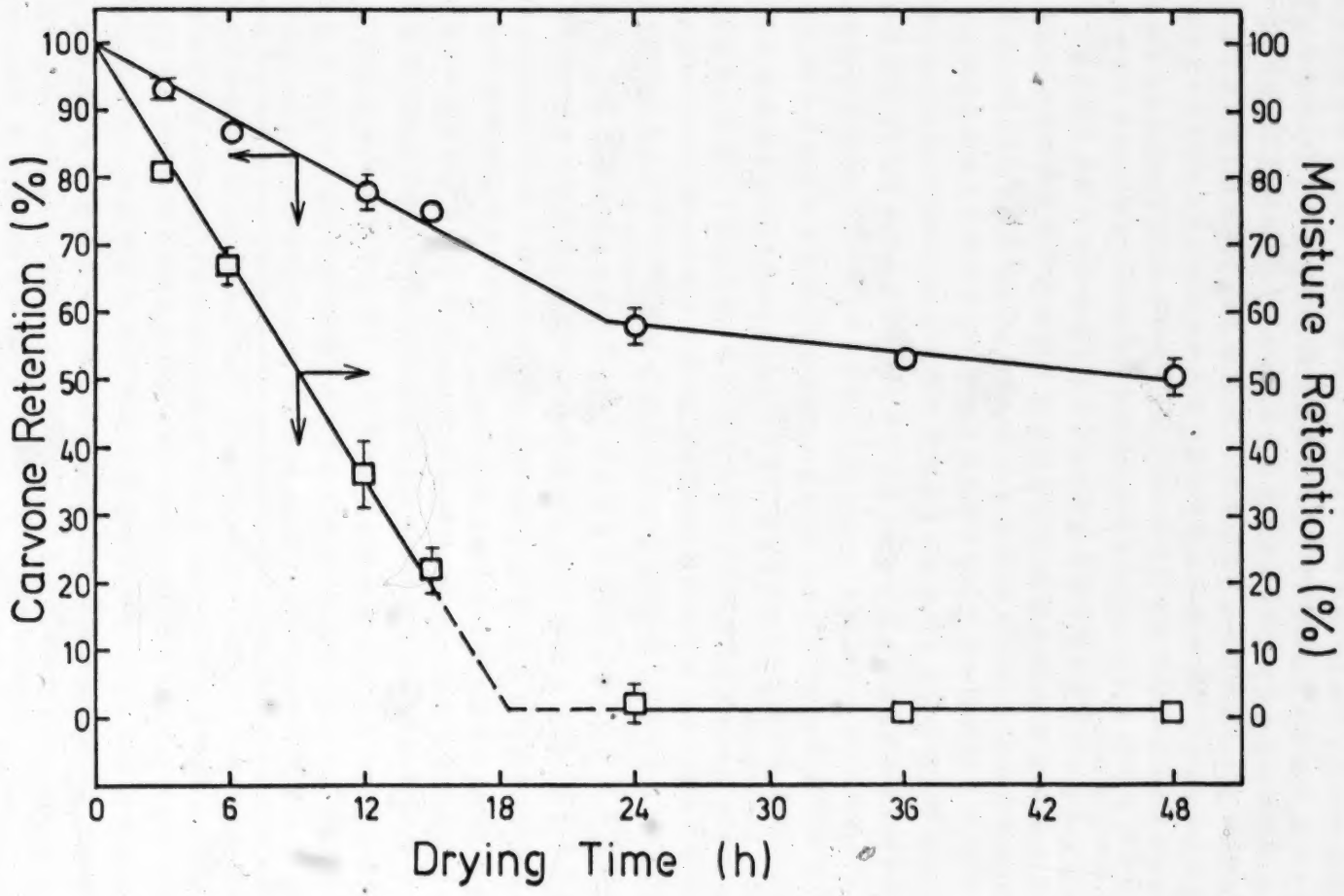


Figure 22. Carvone and moisture retention in gum arabic (1%) as a function of drying time.

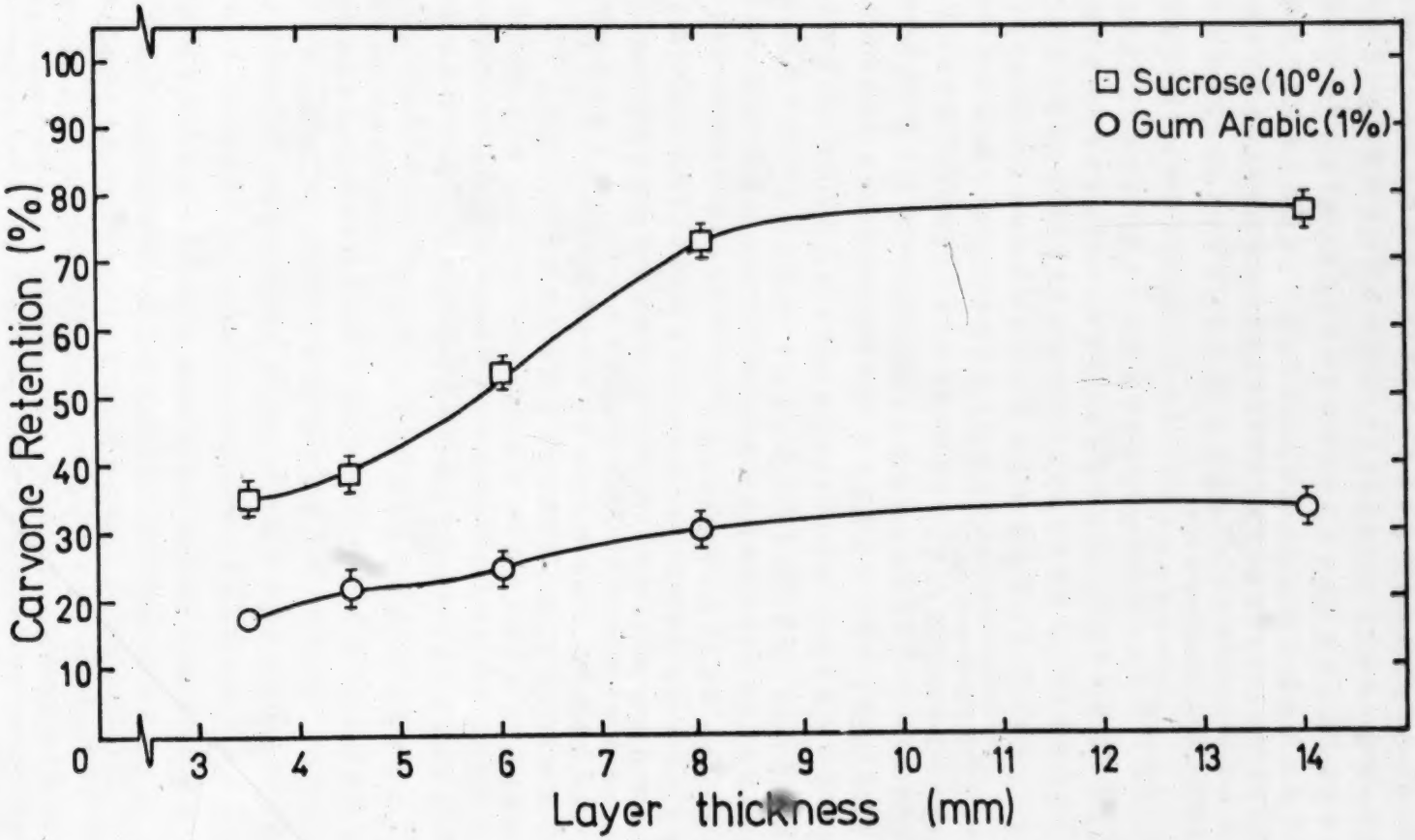


Figure 23. Influence of layer thickness on retention of carvone in sucrose (10%) and gum arabic (1%) at constant sample volume.

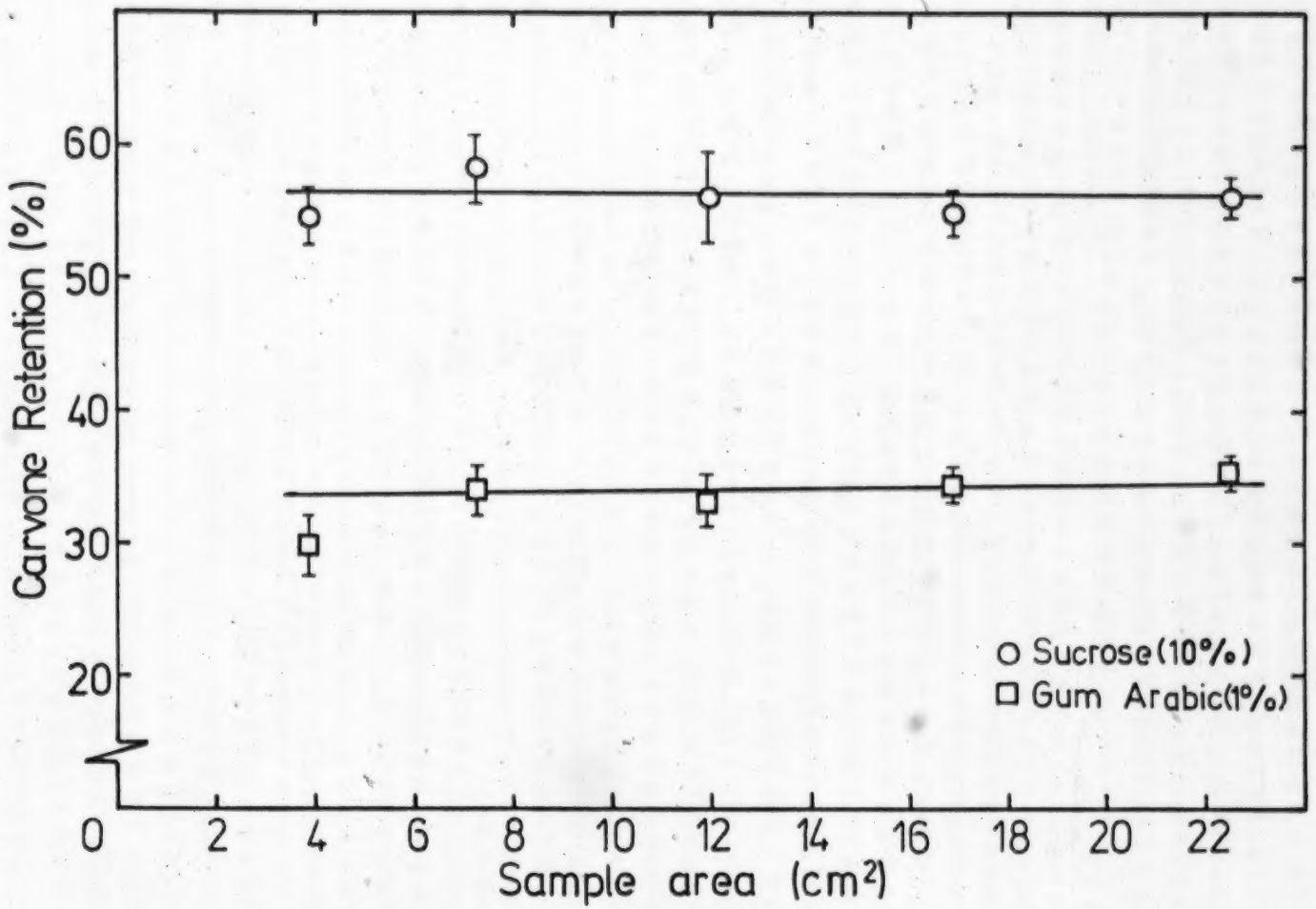


Figure 24. Retention of carvone as a function of surface area in sucrose (10%) and gum arabic (1%) at constant sample thickness.

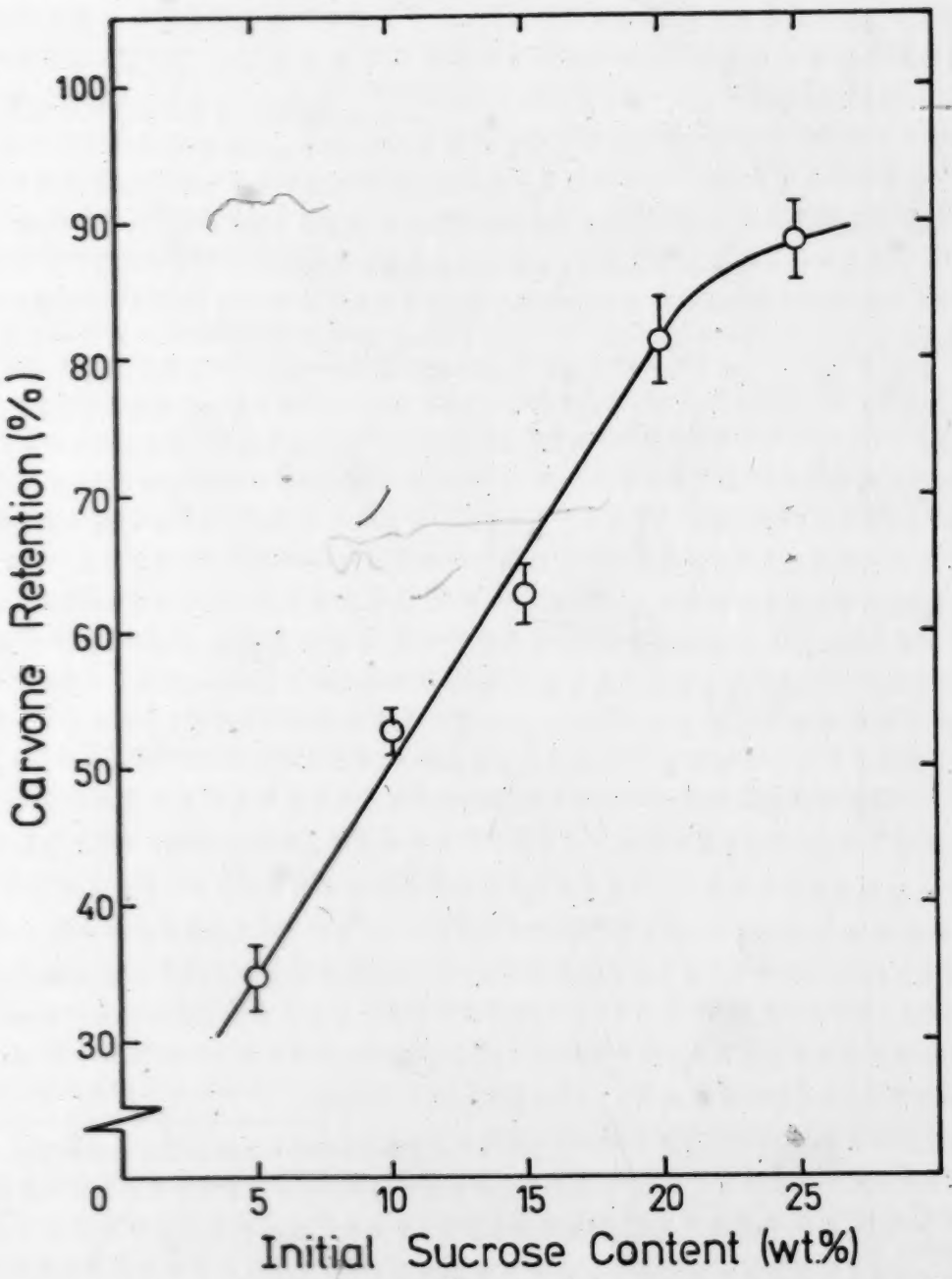


Figure 25. Retention of carvone as a function of initial sucrose content.

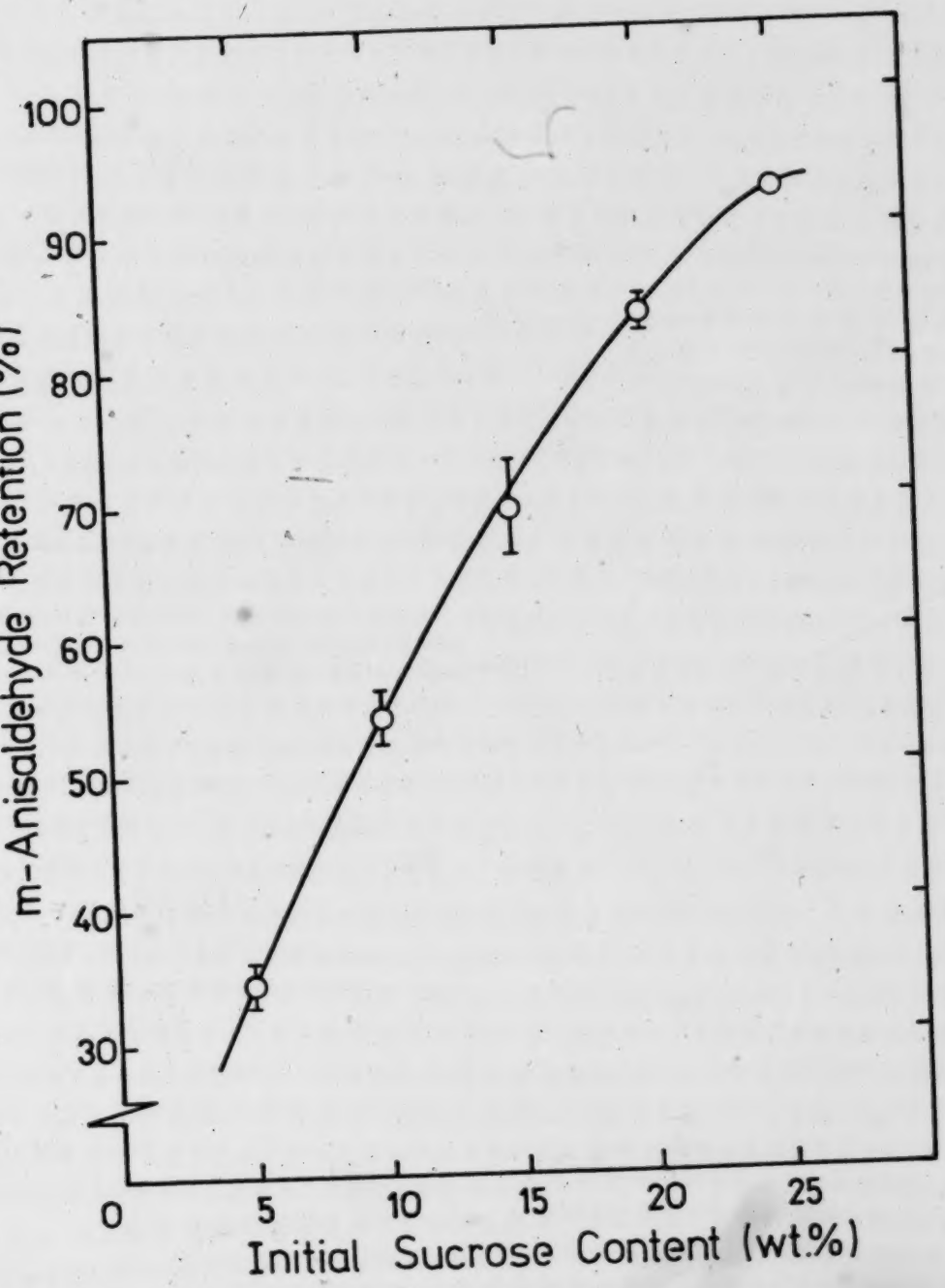


Figure 26. Retention of m-anisaldehyde as a function of initial sucrose content.

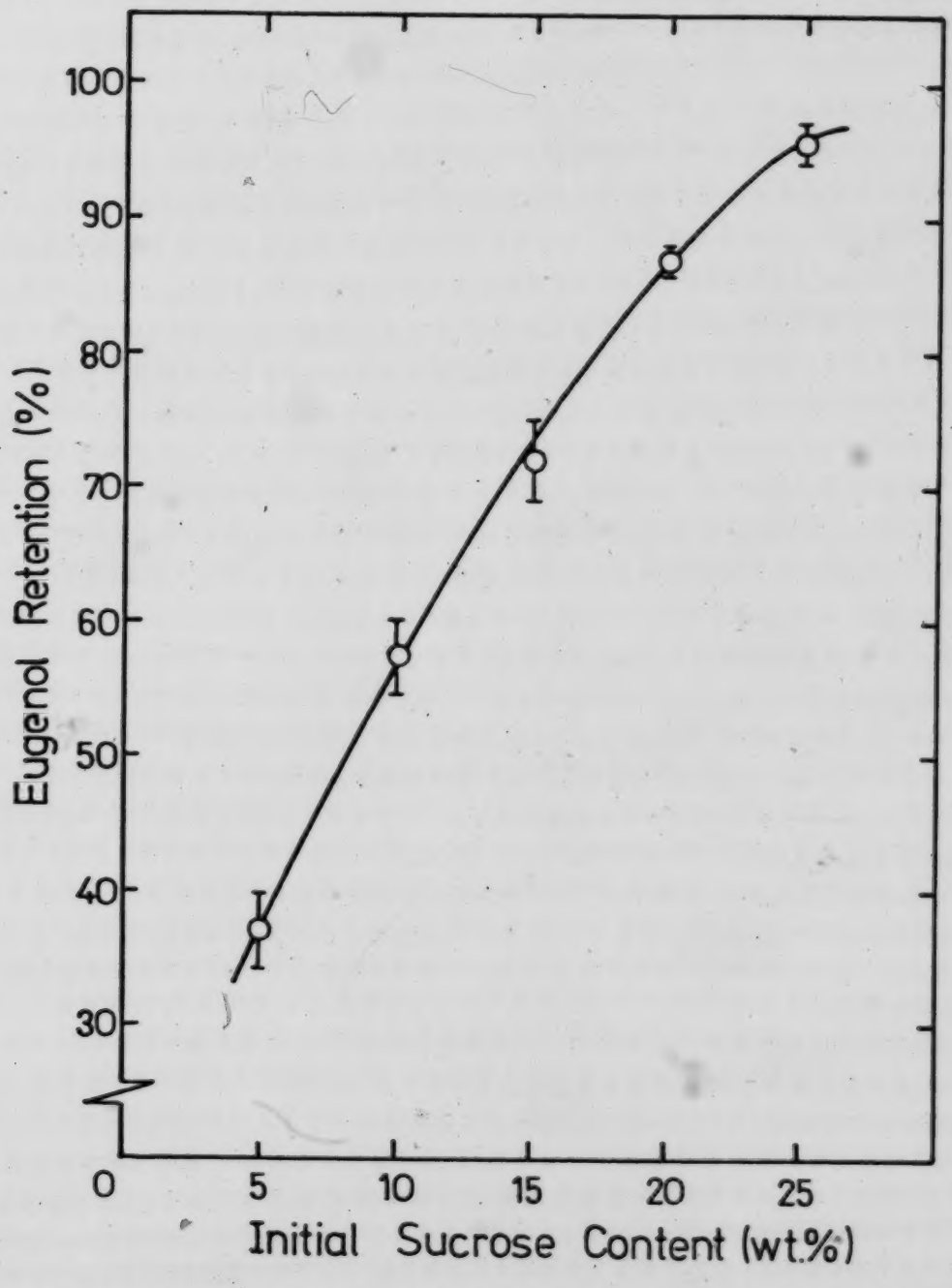


Figure 27. Retention of eugenol as a function of initial sucrose content.

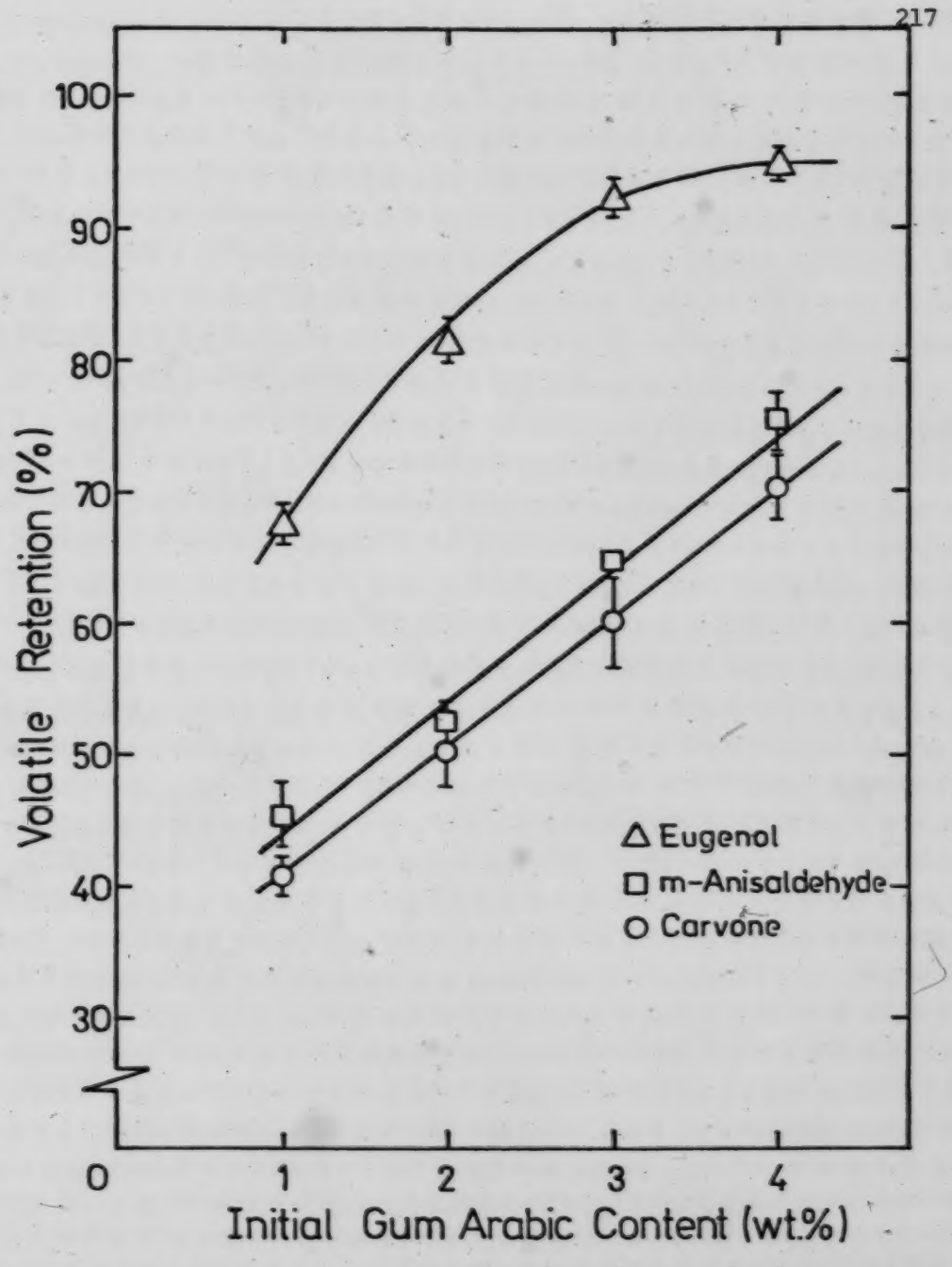


Figure 28. Retention of carvone, m-anisaldehyde and eugenol as a function of initial gum arabic content.

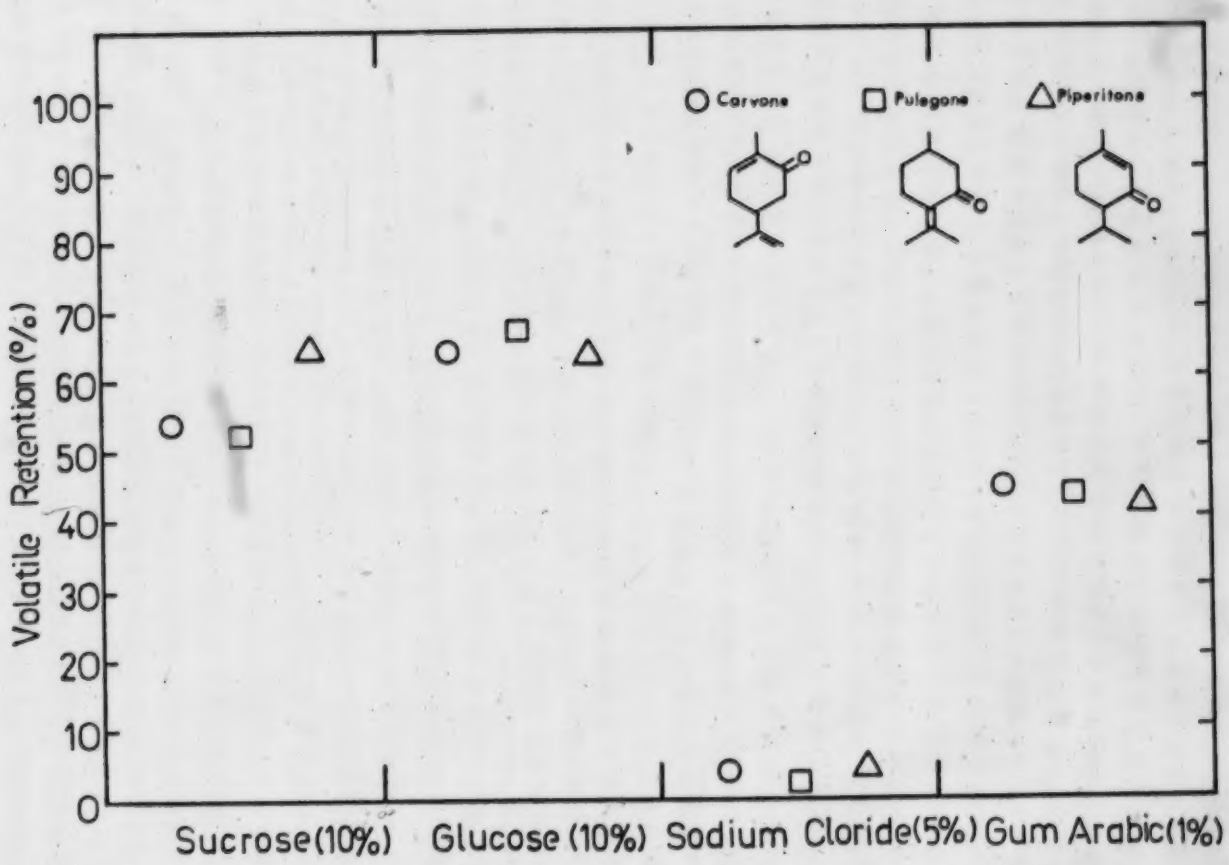


Figure 29. Retention of carvone, pulegone and piperitone in sucrose, glucose, sodium chloride and gum arabic solutions.

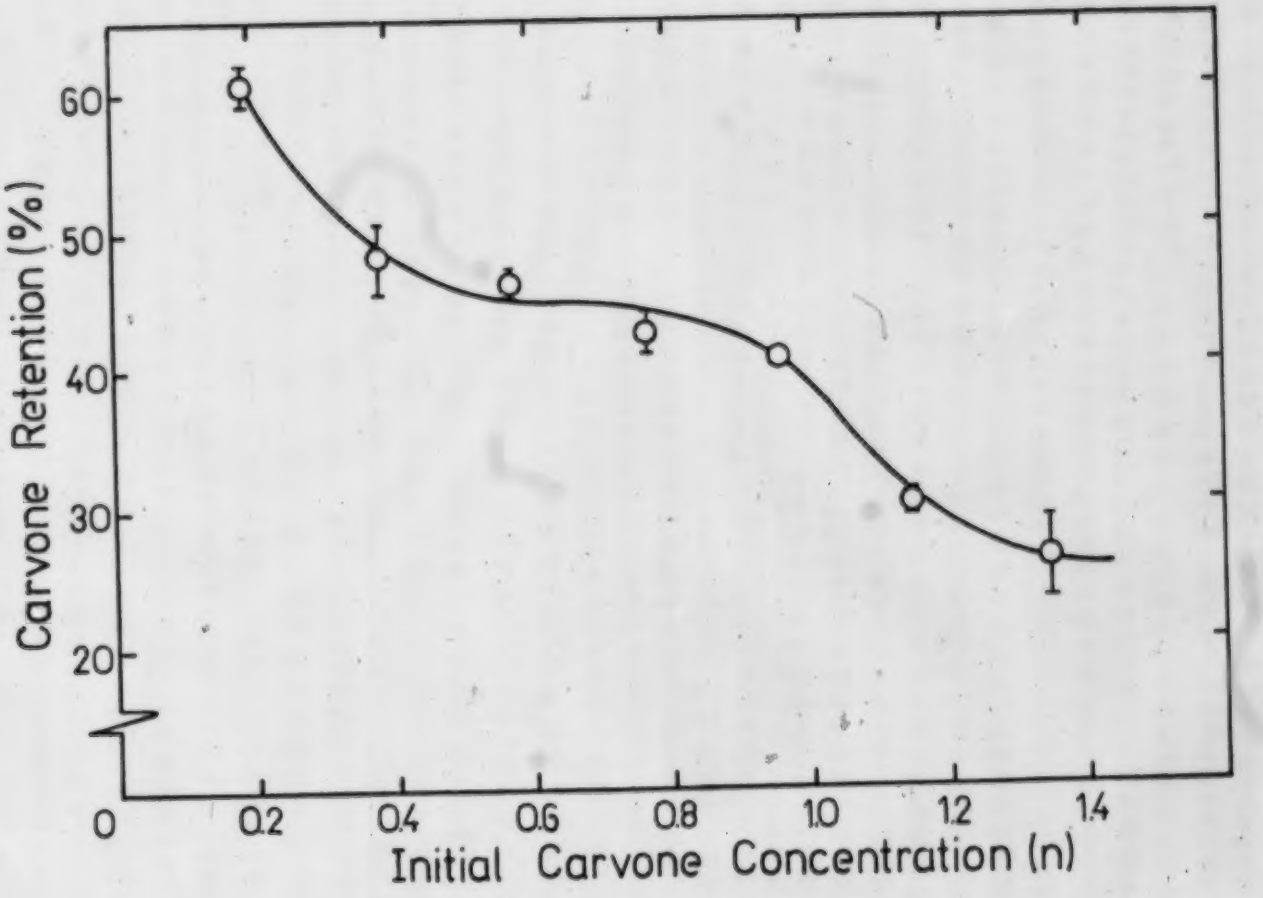


Figure 30. Carvone retention as a function of initial carvone concentration in 10% sucrose.

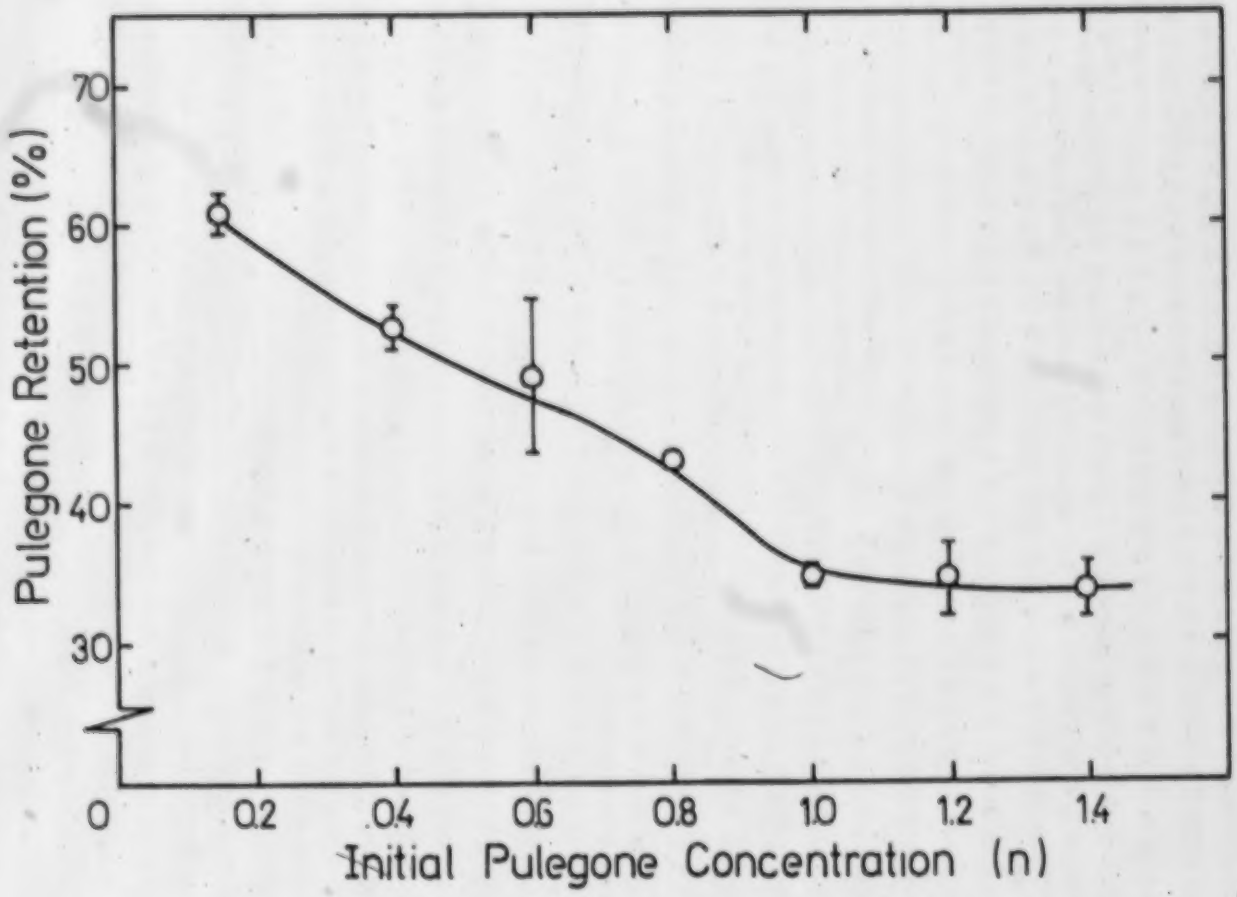


Figure 31. Pulegone retention as a function of initial pulegone concentration in 10% sucrose.

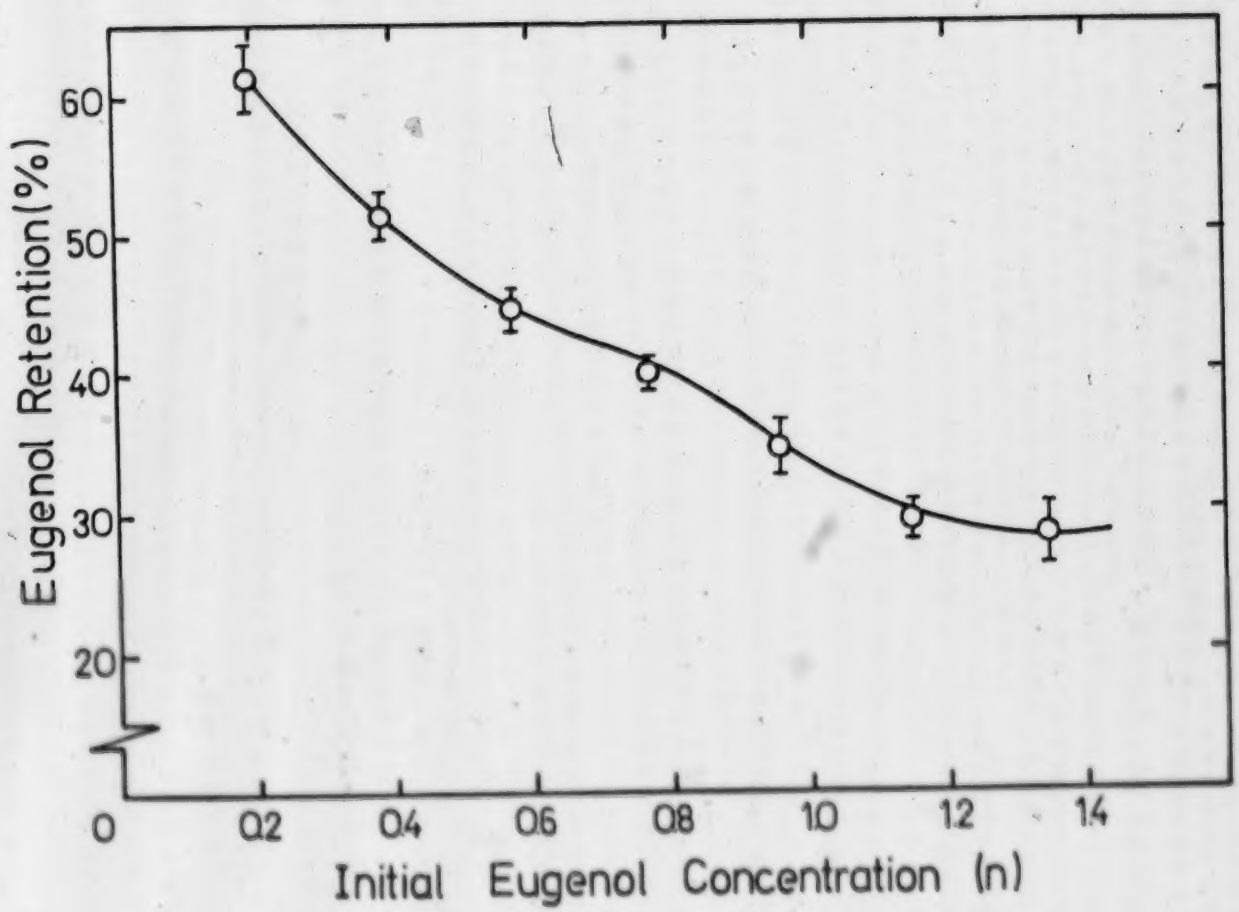


Figure 32. Eugenol retention as a function of initial eugenol concentration in 10% sucrose.

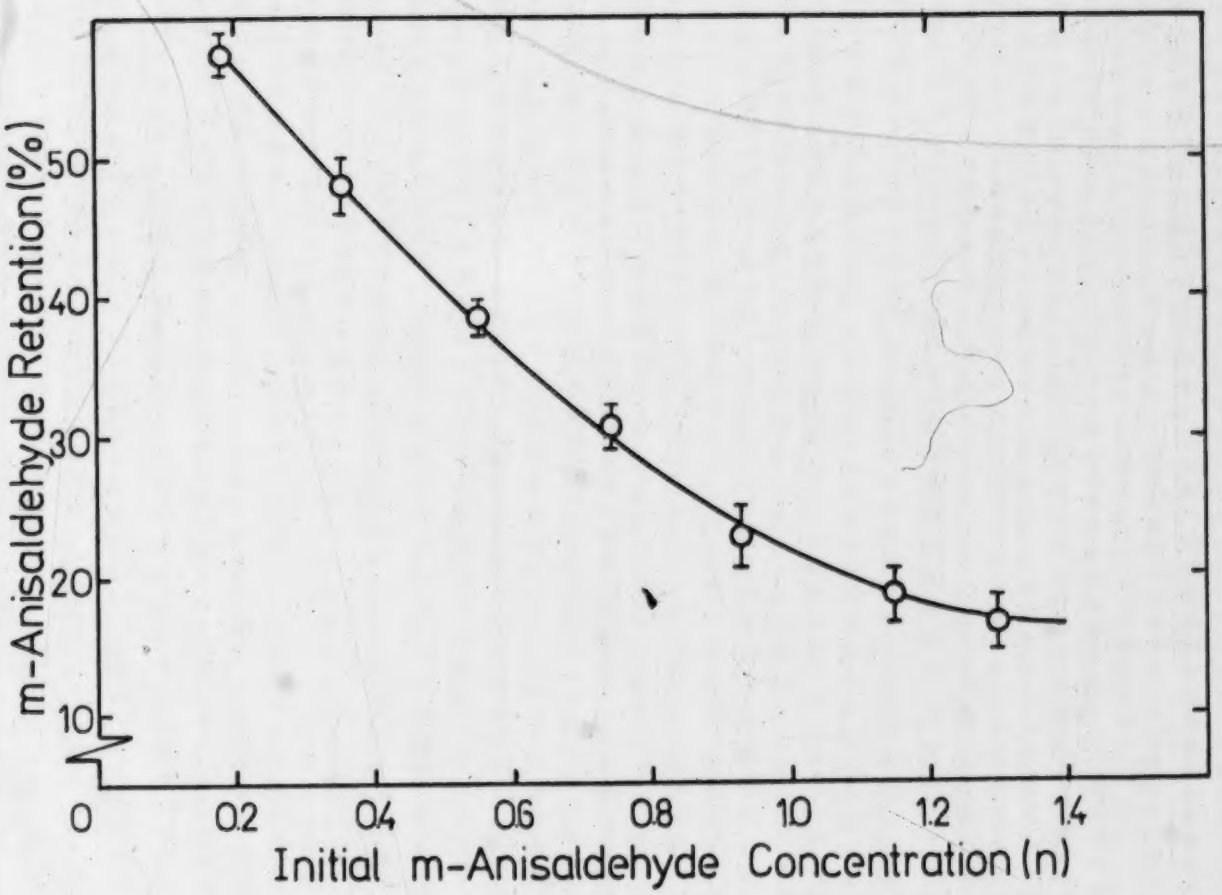


Figure 33. m-Anisaldehyde retention as a function of initial m-anisaldehyde concentration in 10% sucrose.

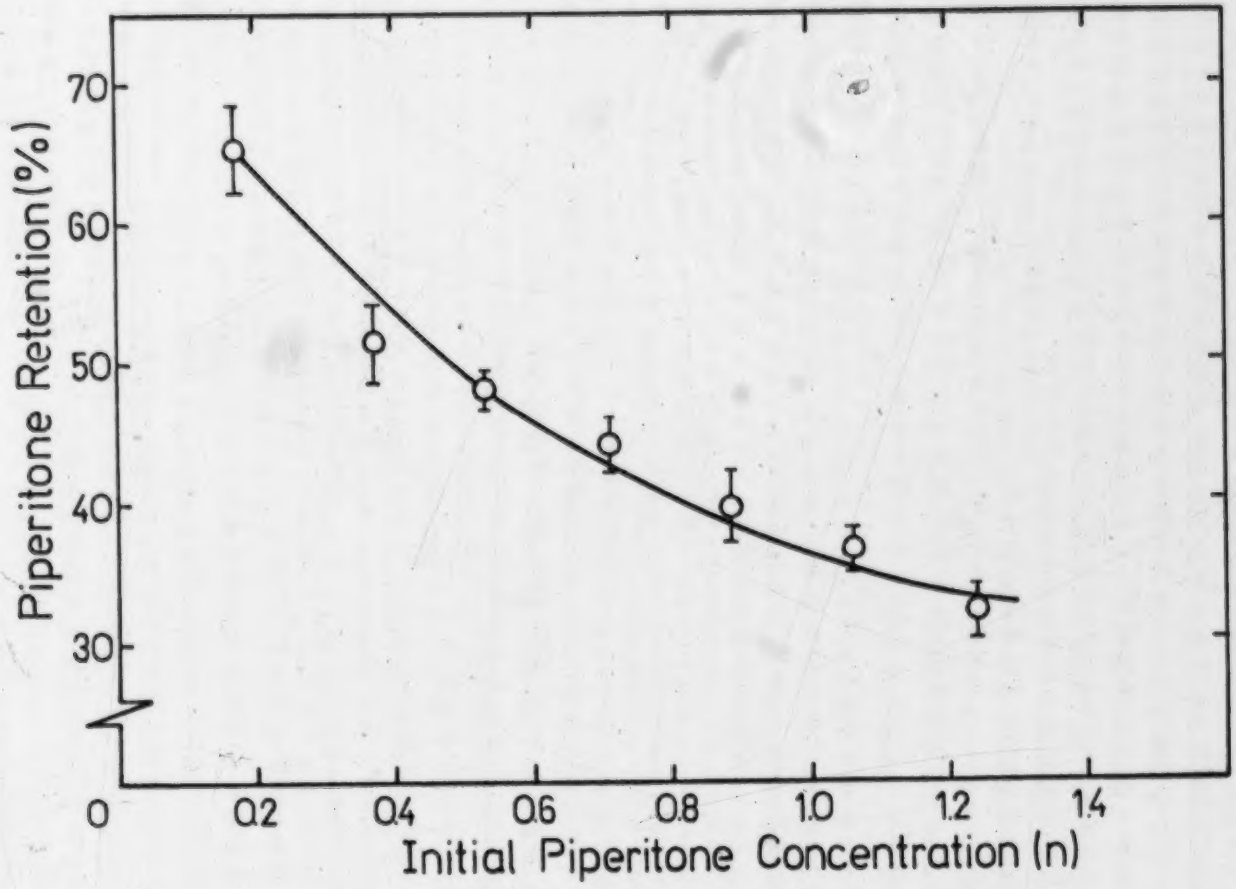


Figure 34. Piperitone retention as a function of initial piperitone concentration in 10% sucrose.

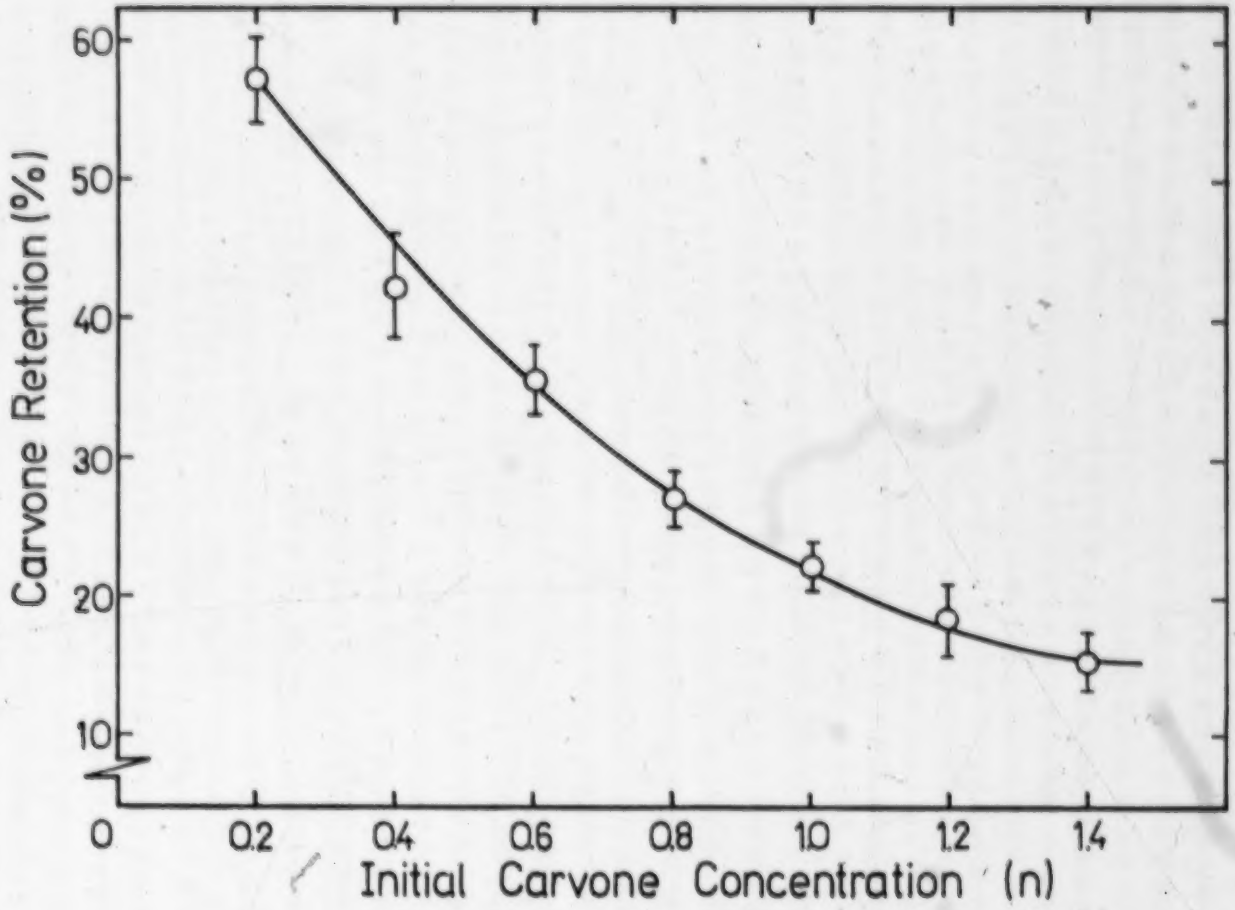


Figure 35. Carvone retention in 1% gum arabic as a function of initial carvone concentration.

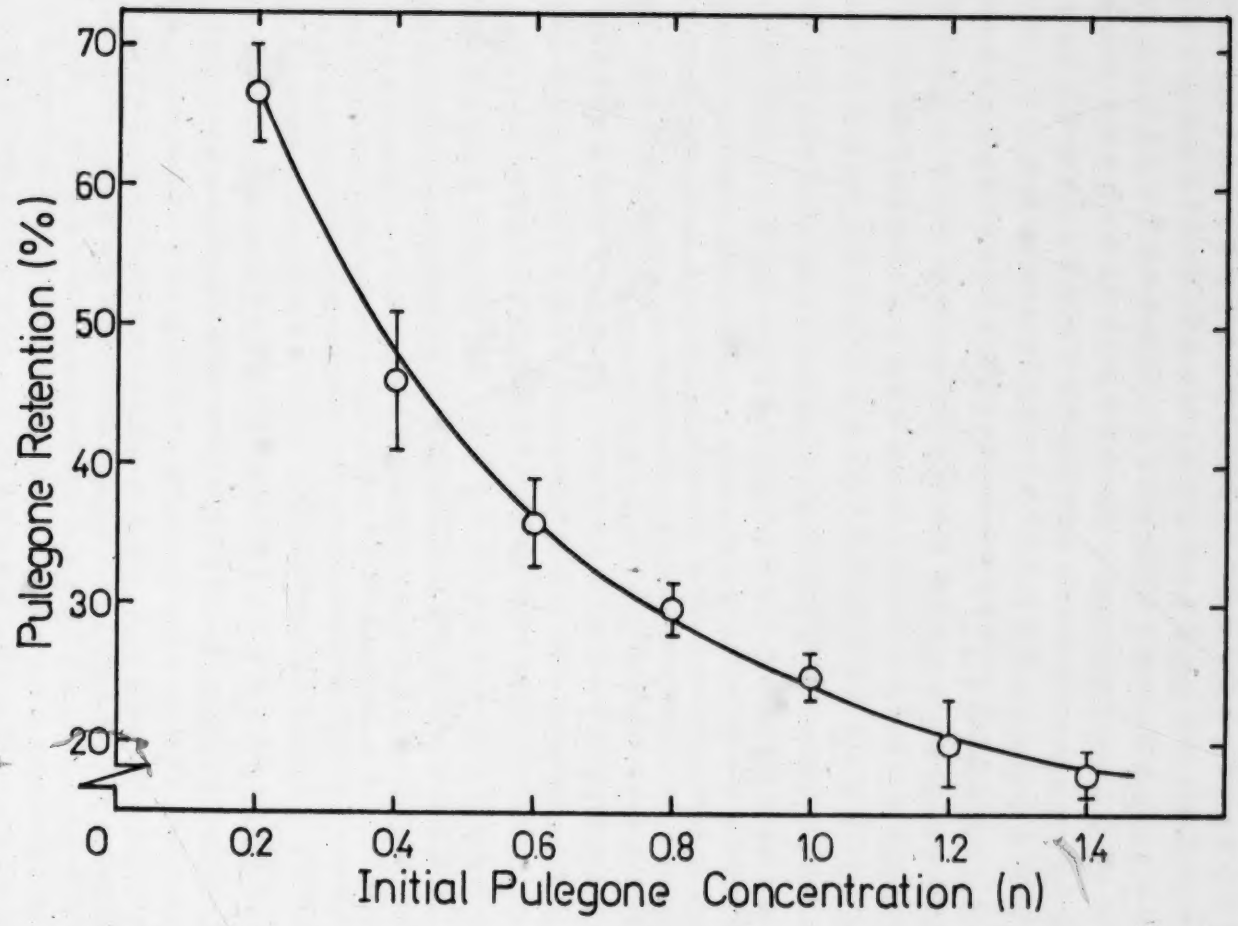


Figure 36. Pulegone retention in 1% gum arabic as a function of initial pulegone concentration.

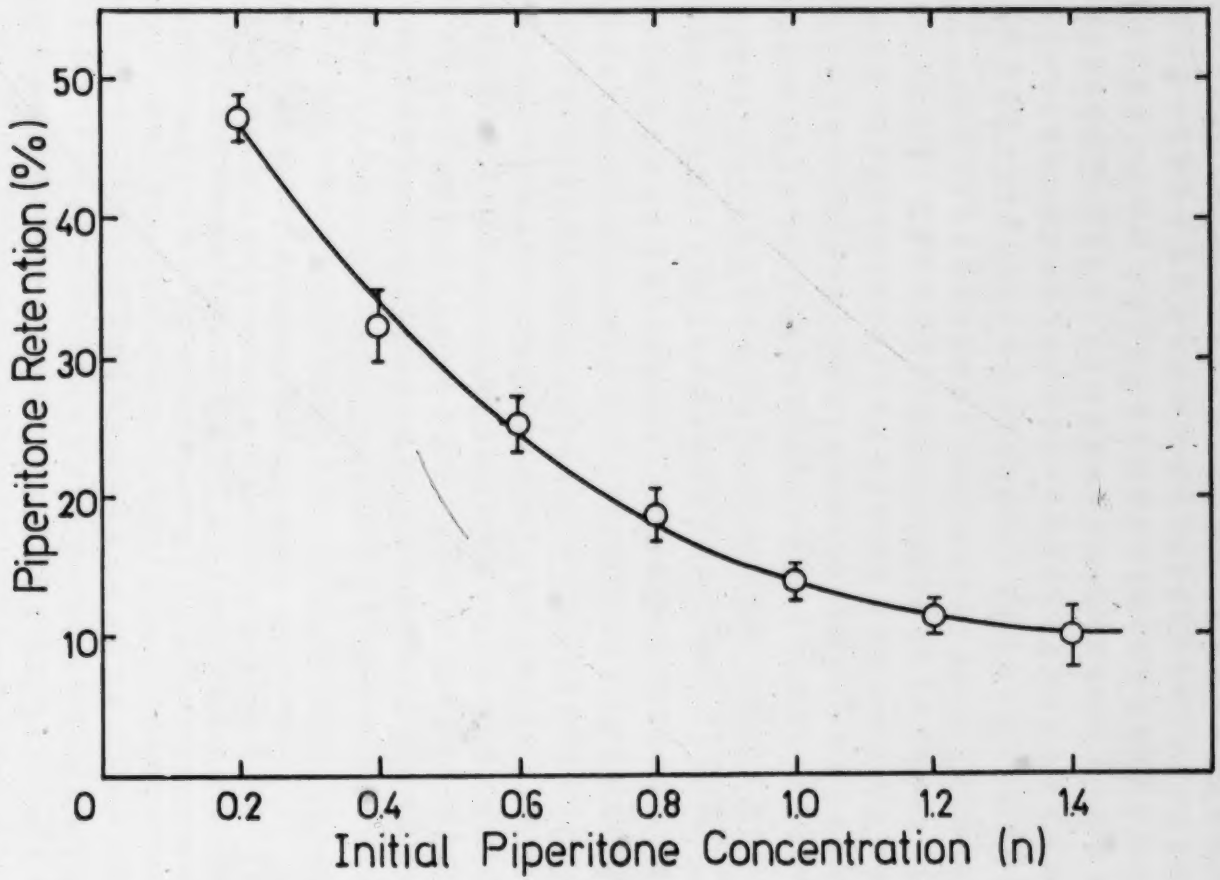


Figure 37. Piperitone retention in 1% gum arabic as a function of initial piperitone concentration.

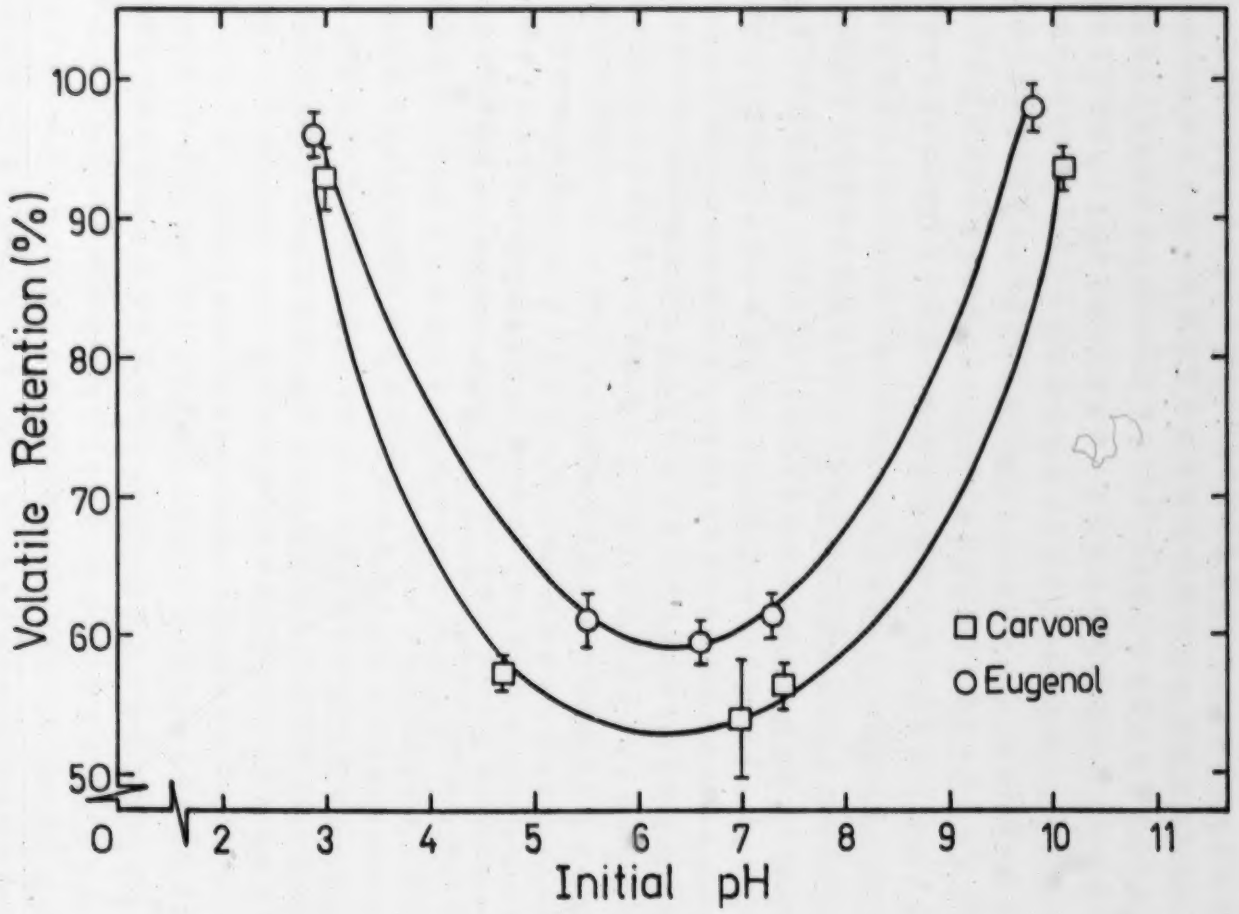


Figure 38. Variation of carvone and eugenol retention in 10% sucrose as a function of initial pH.

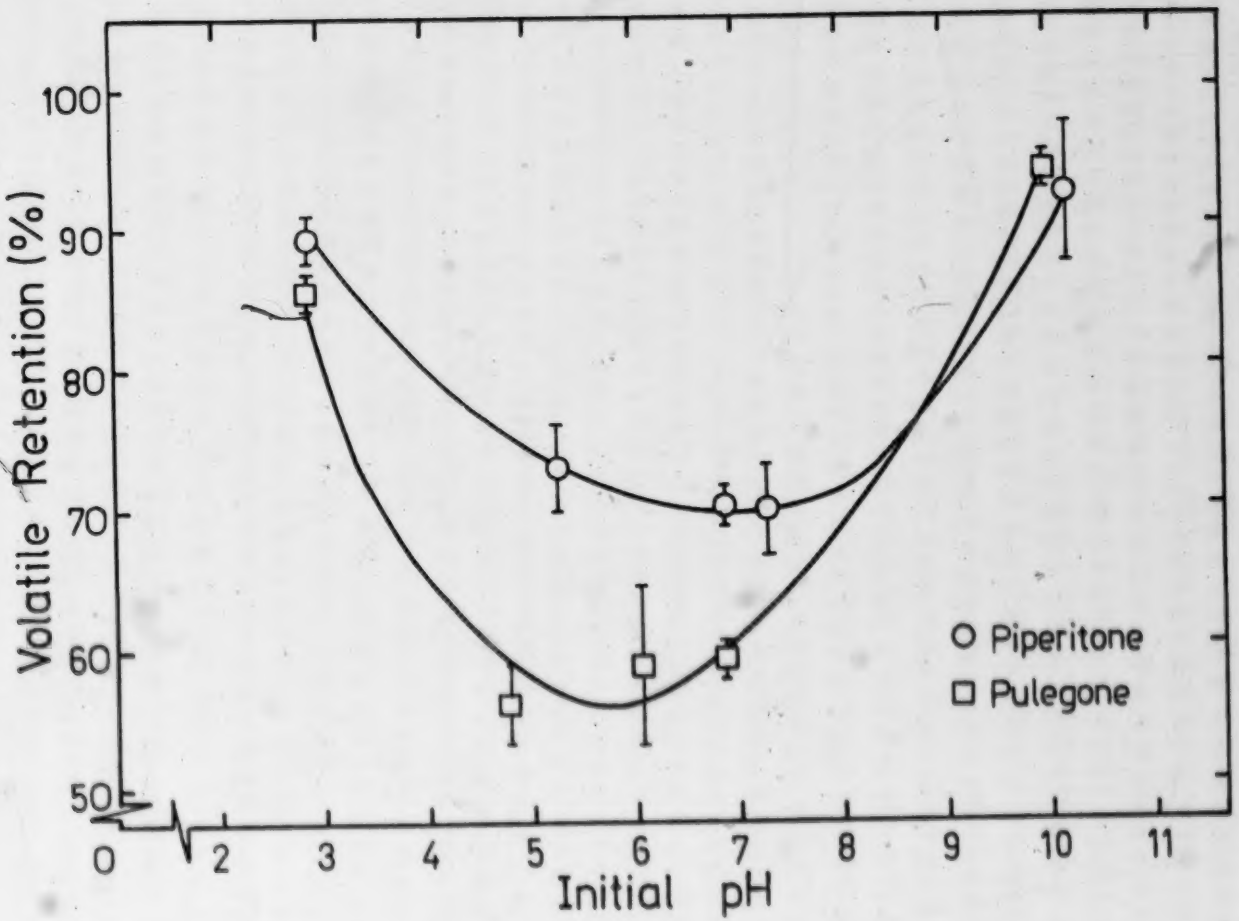


Figure 39. Piperitone and pulegone retention in 10% sucrose as a function of initial pH.

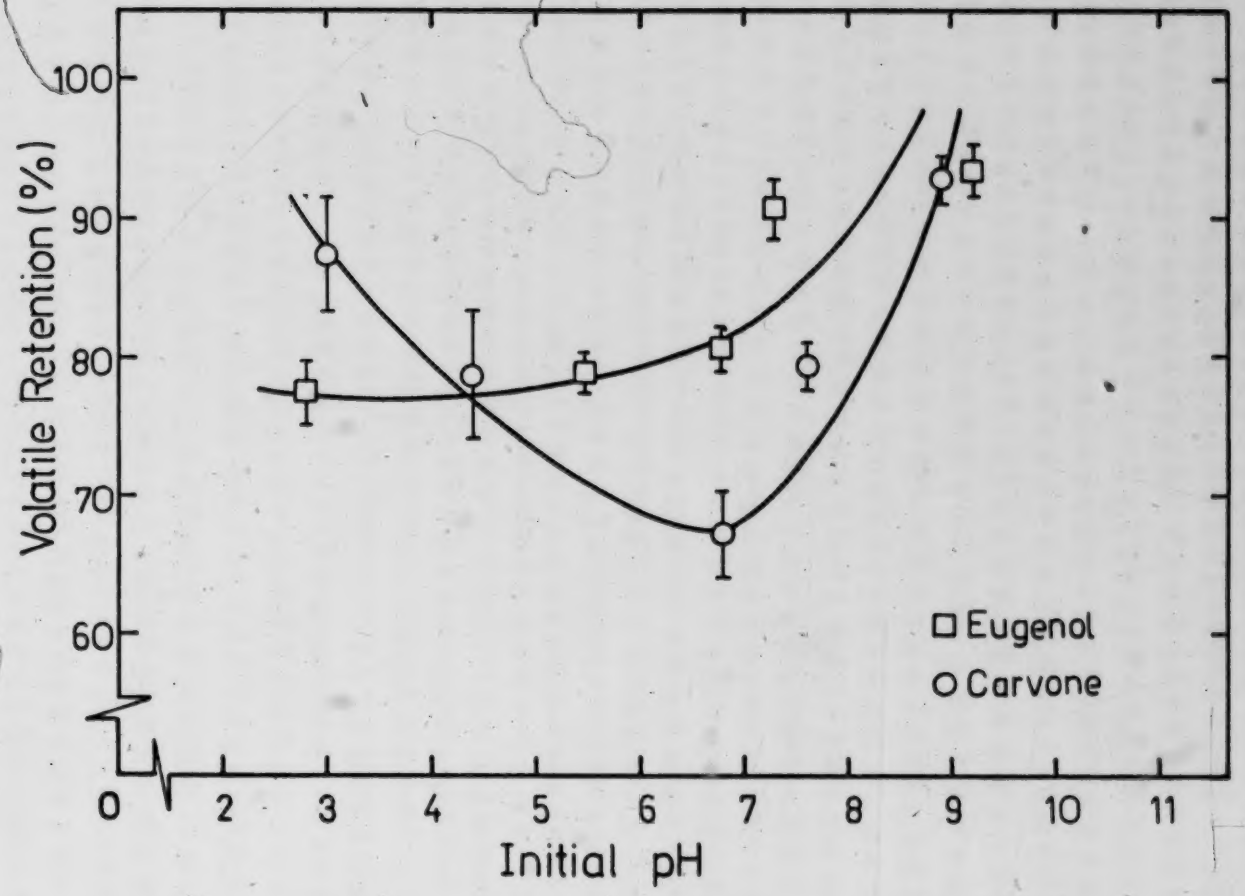


Figure 40. Carvone and eugenol retention in 10% glucose as a function of initial pH.

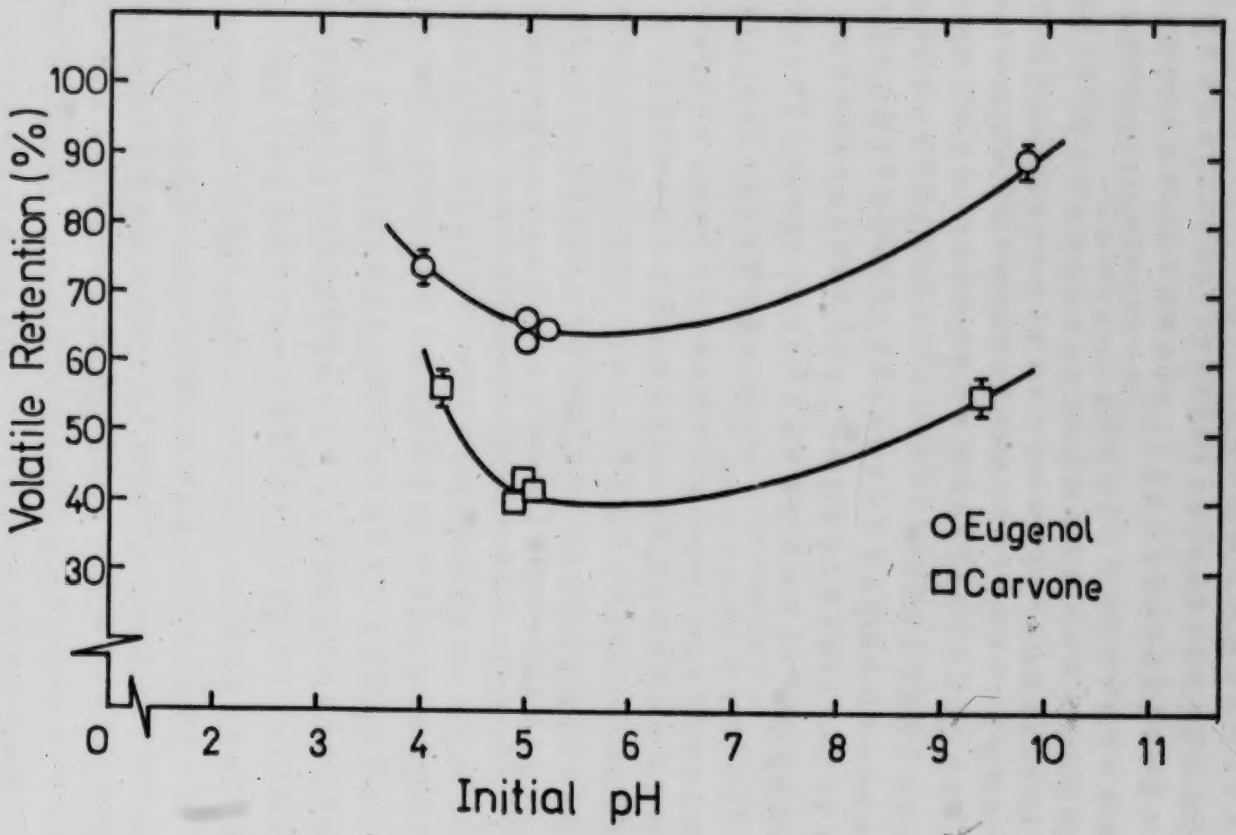


Figure 41. Retention of carvone and eugenol in 1% gum arabic as a function of initial pH.

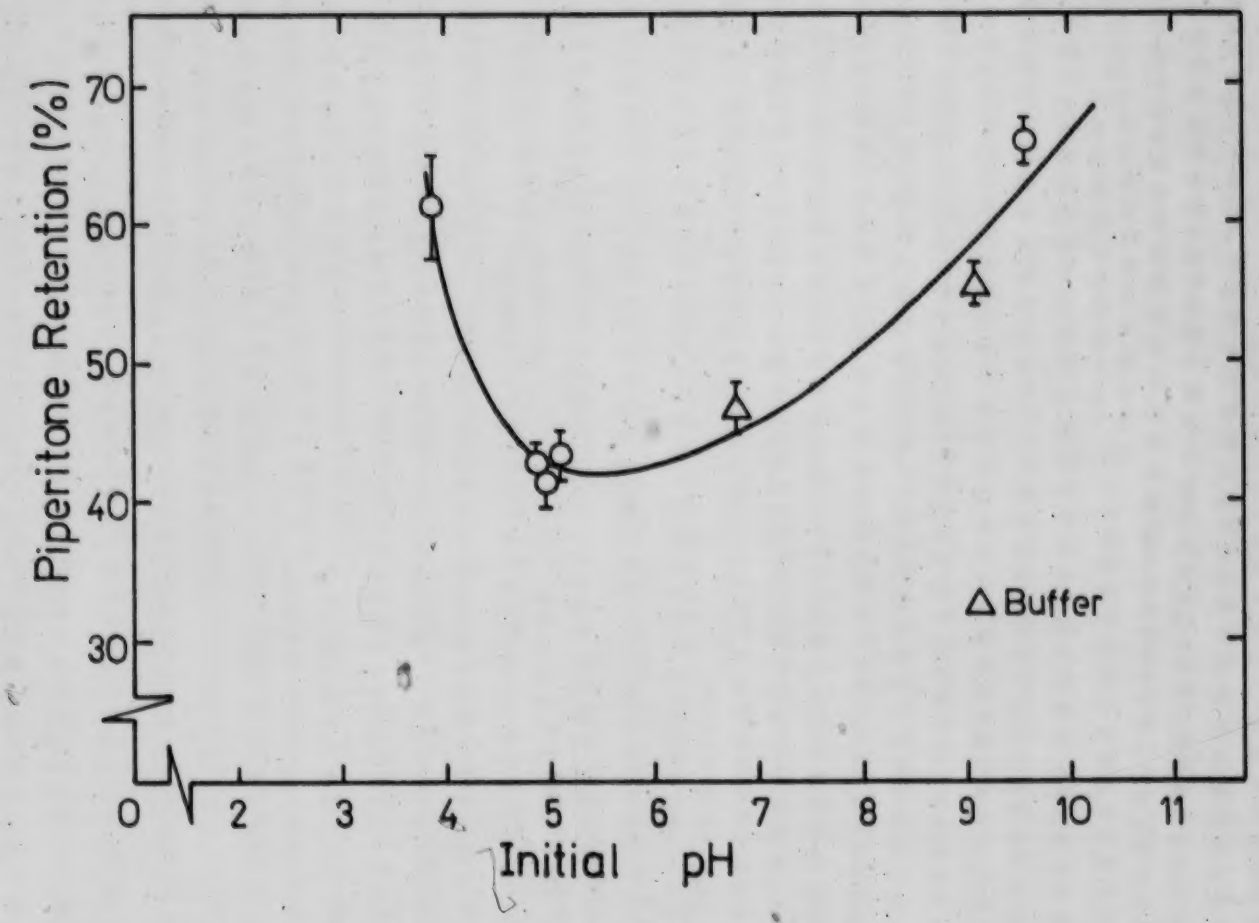


Figure 42. Piperitone retention in 1% gum arabic as a function of initial pH.

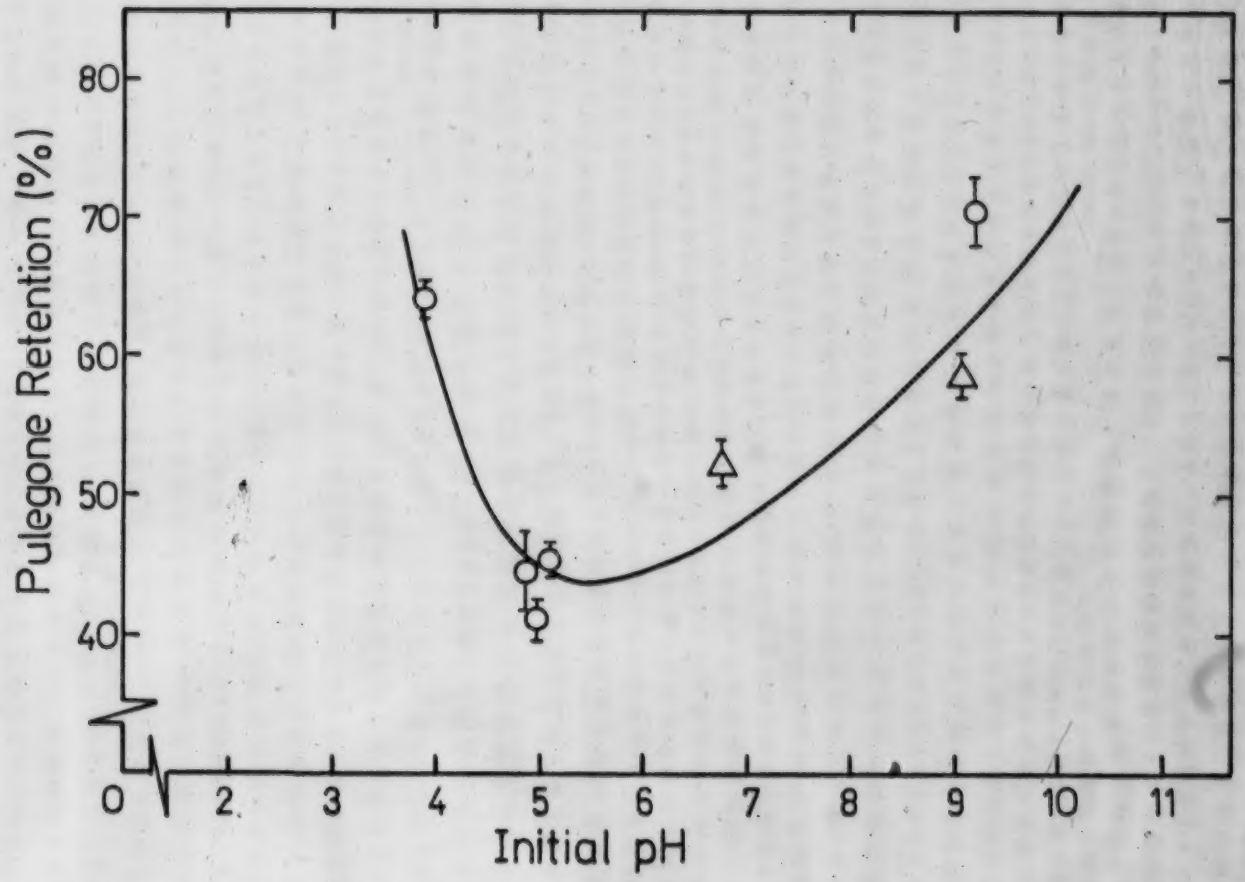


Figure 43. Pulegone retention in 1% gum arabic as a function of initial pH.

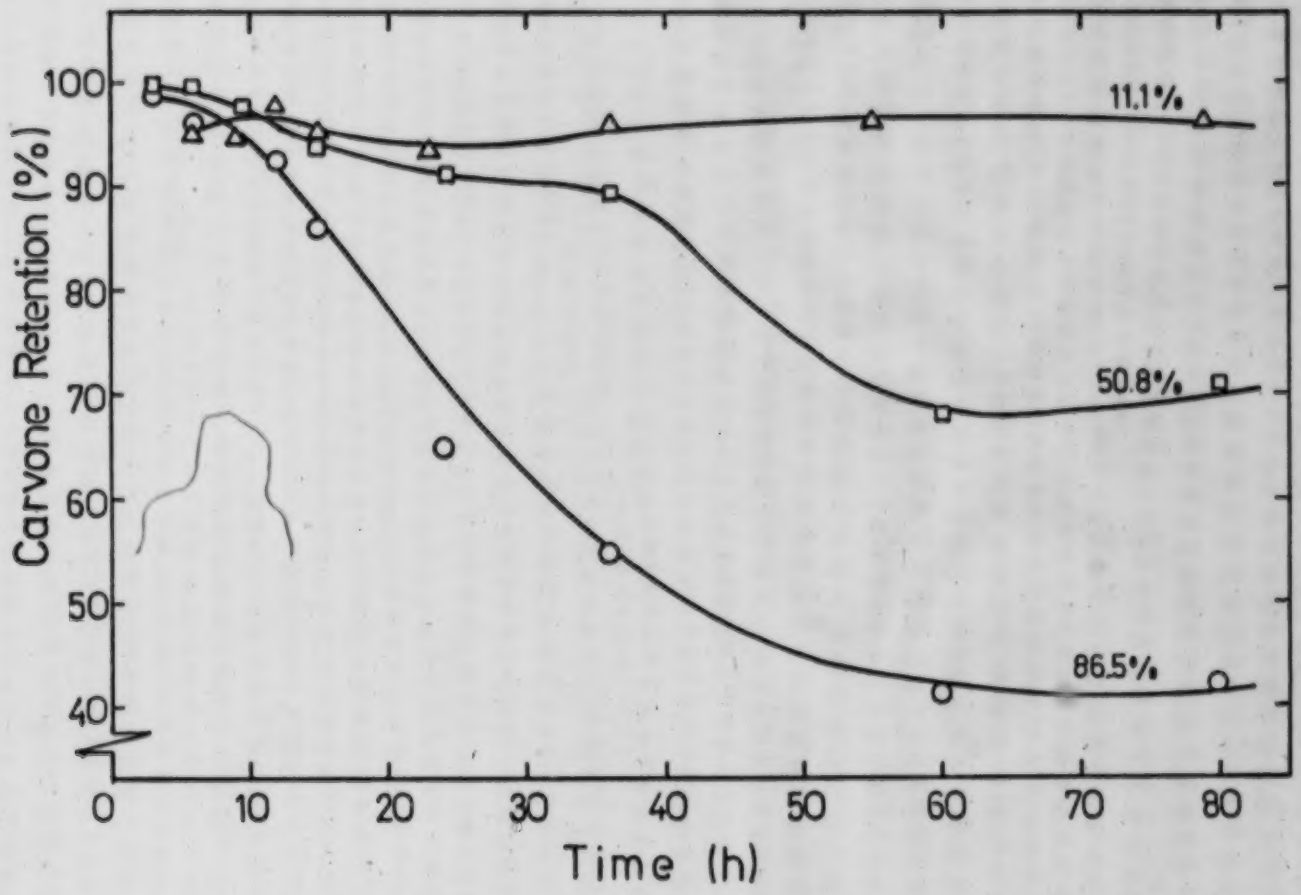


Figure 44. Retention of carvone after rehumidification of freeze-dried sucrose solutions at different relative humidities.

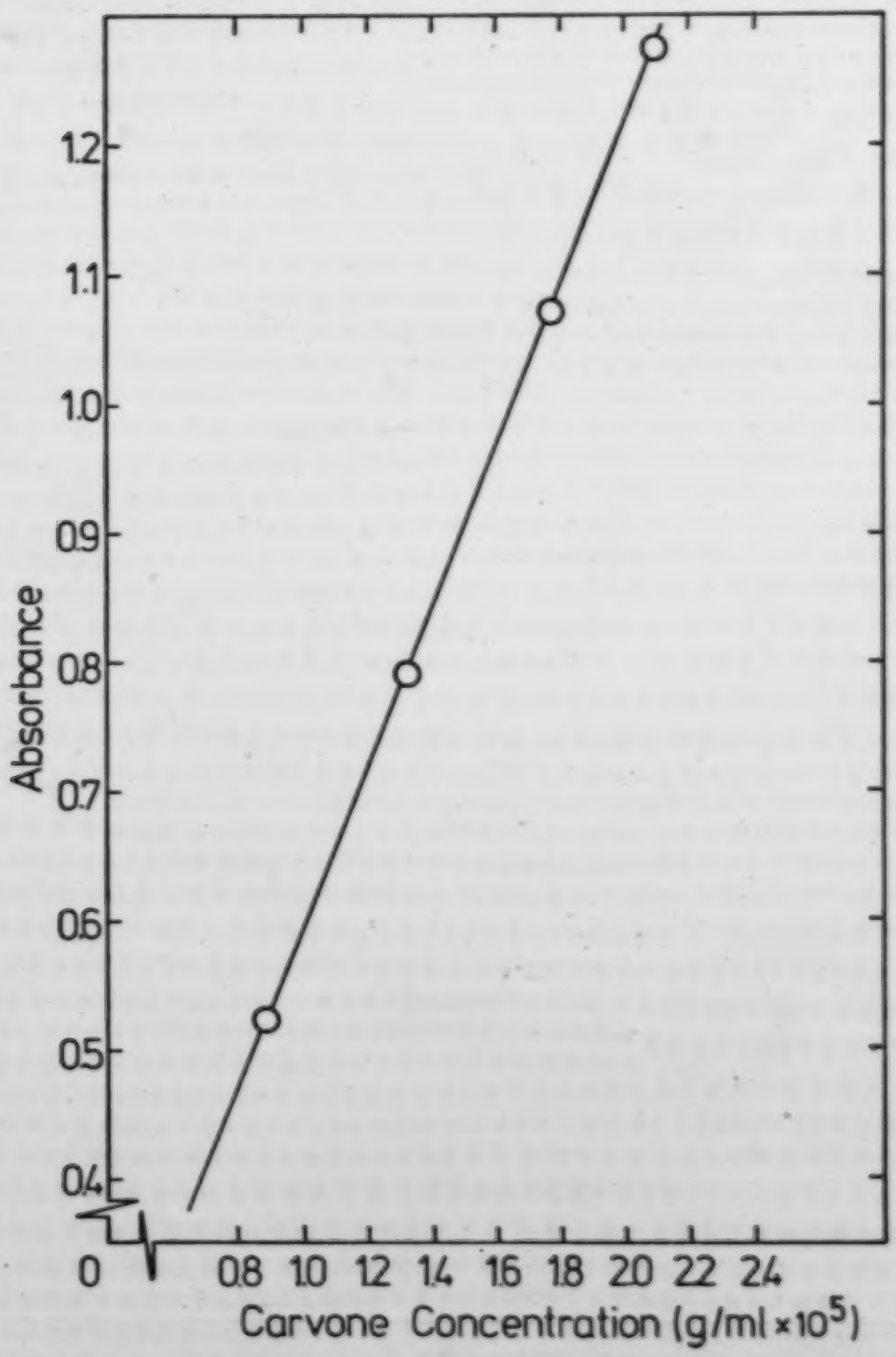


Figure 45. Standard curve for carvone in water at λ=241.5 nm.

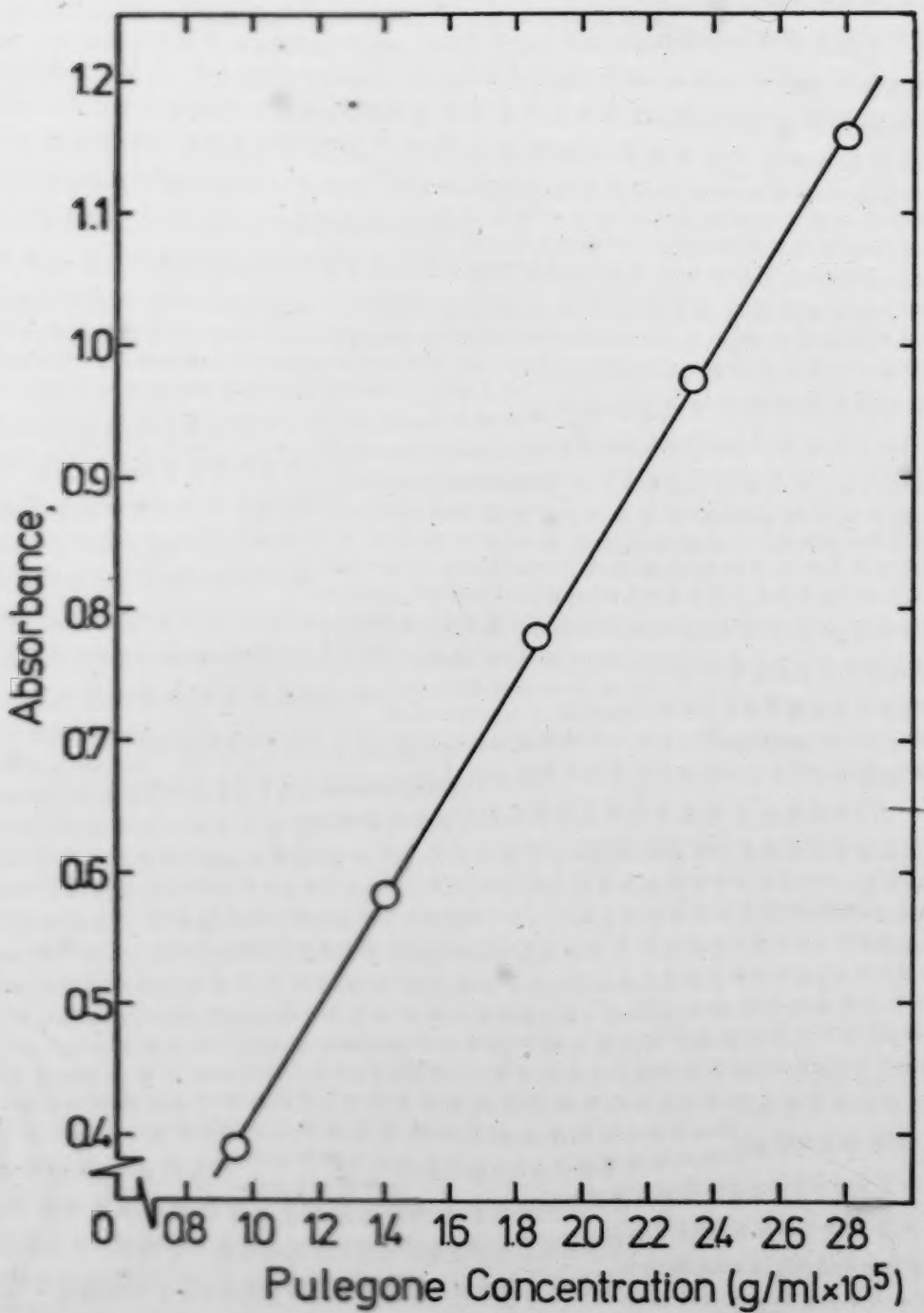


Figure 46. Standard curve for pulegone in water at λ=263.0 nm.

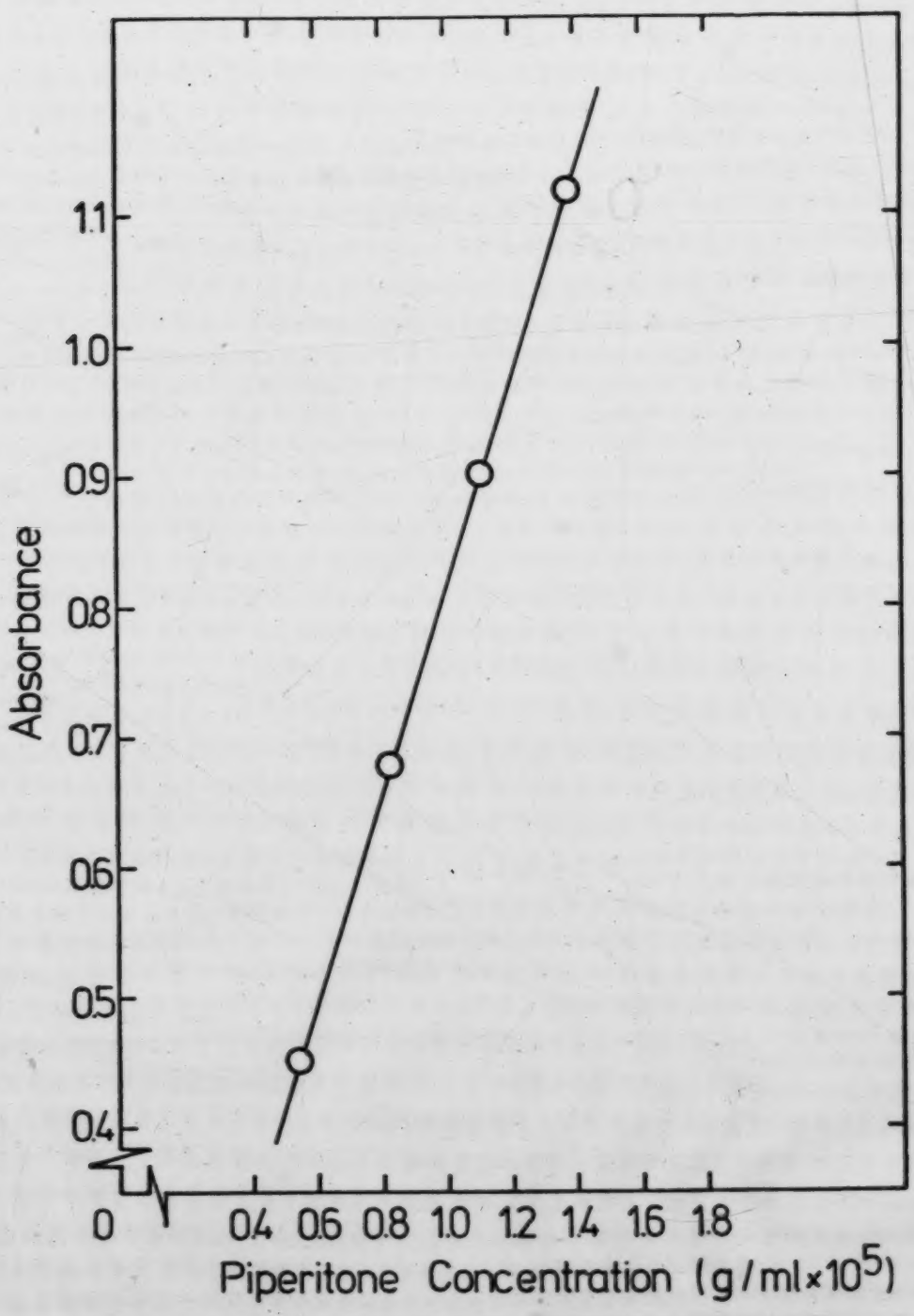


Figure 47. Standard curve for piperitone in water at λ=242.5 nm.

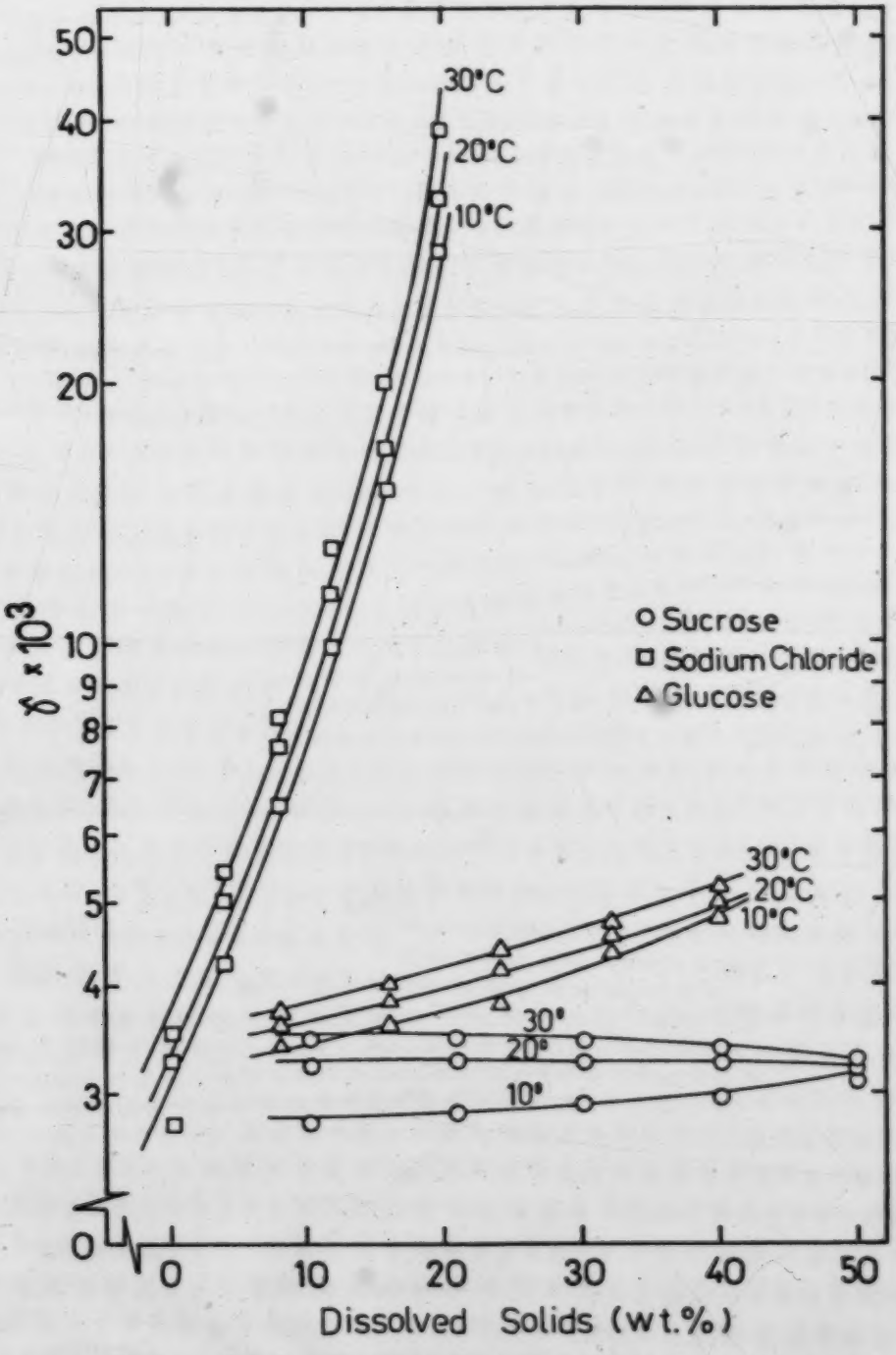


Figure 48. Activity coefficients of piperitone as a function of temperature and dissolved solids content.

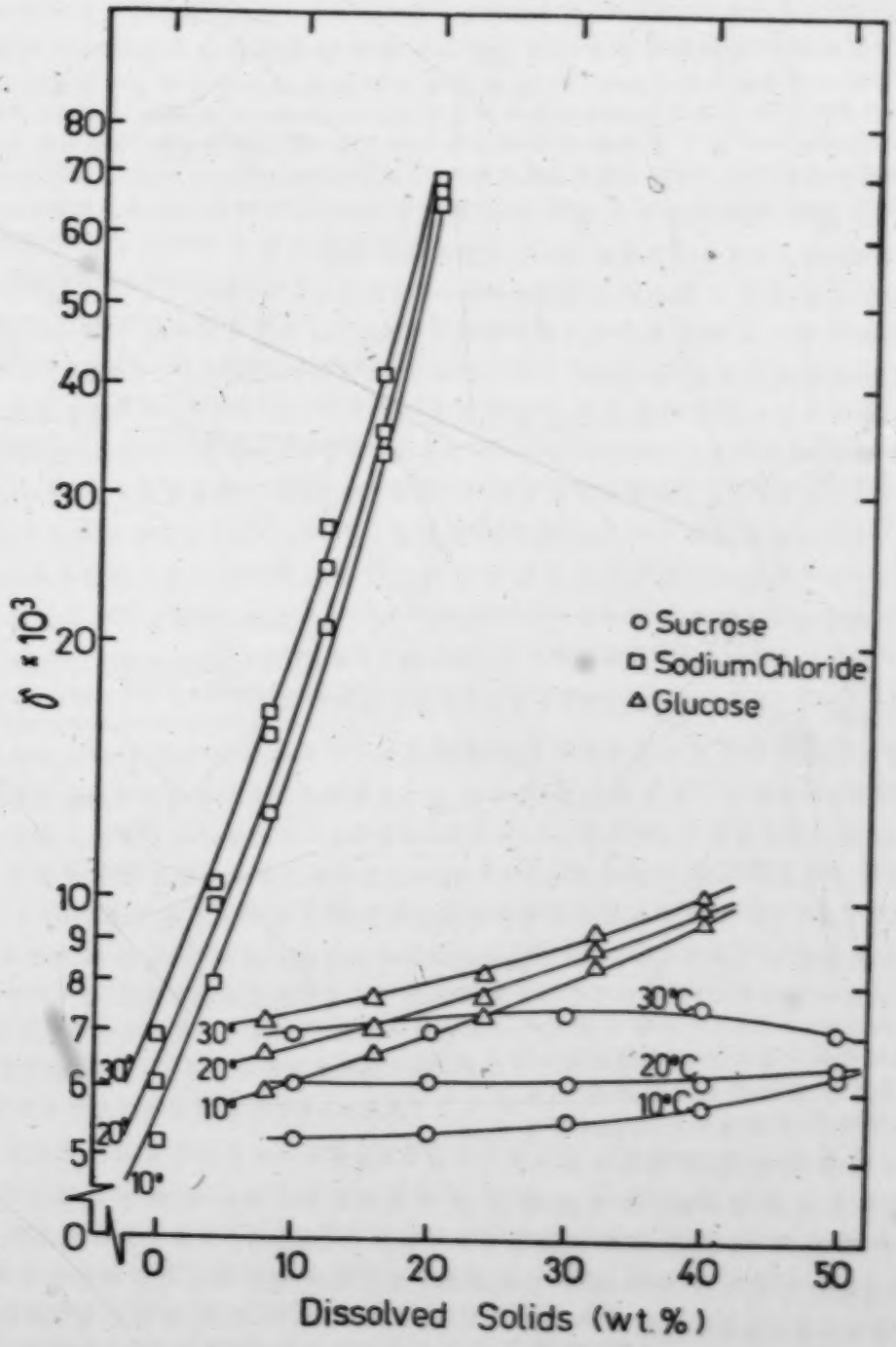


Figure 49. Activity coefficients of pulegone as a function of temperature and dissolved solids content.

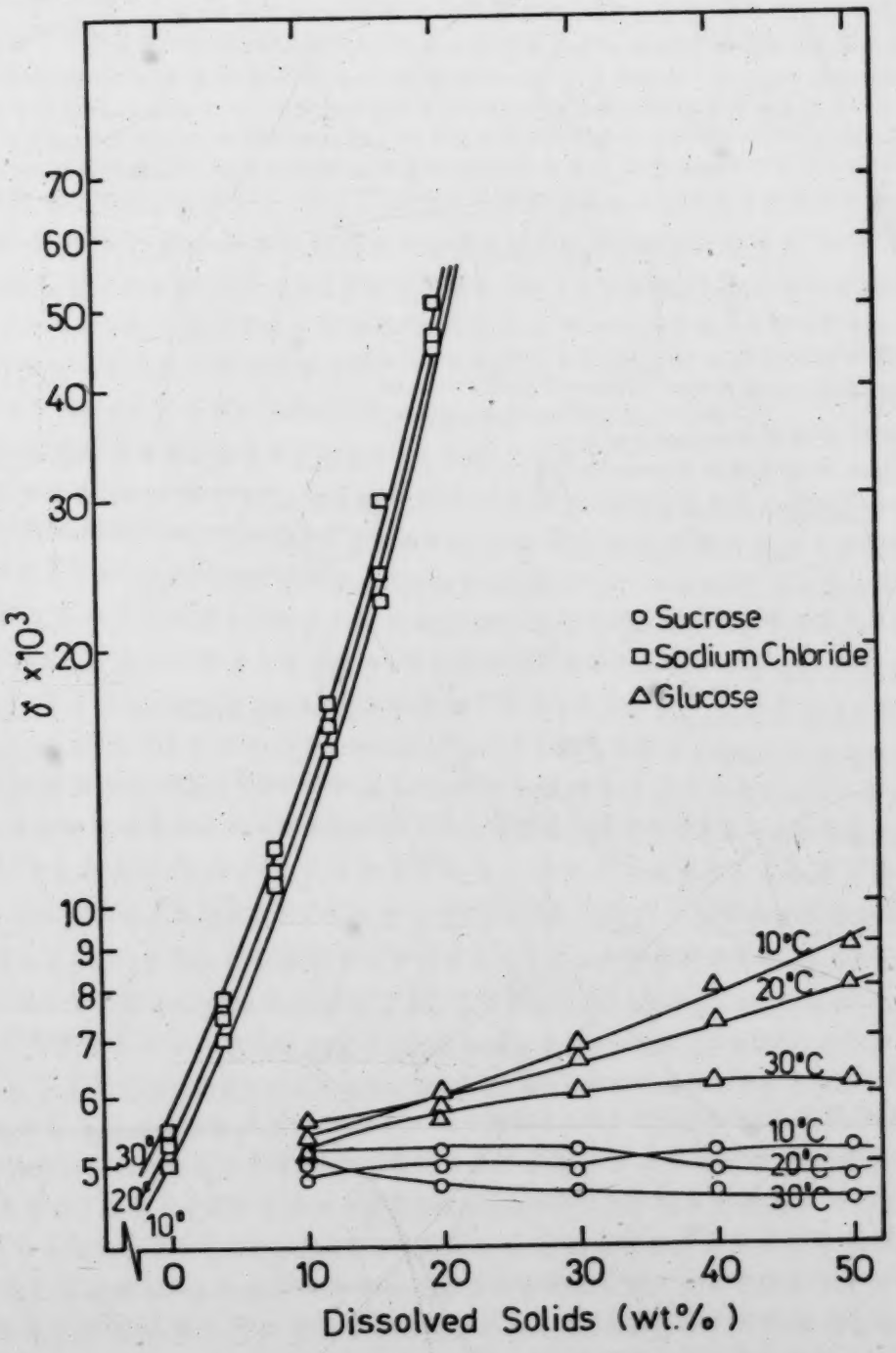


Figure 50. Activity coefficients of carvone as a function of temperature and dissolved solids content.

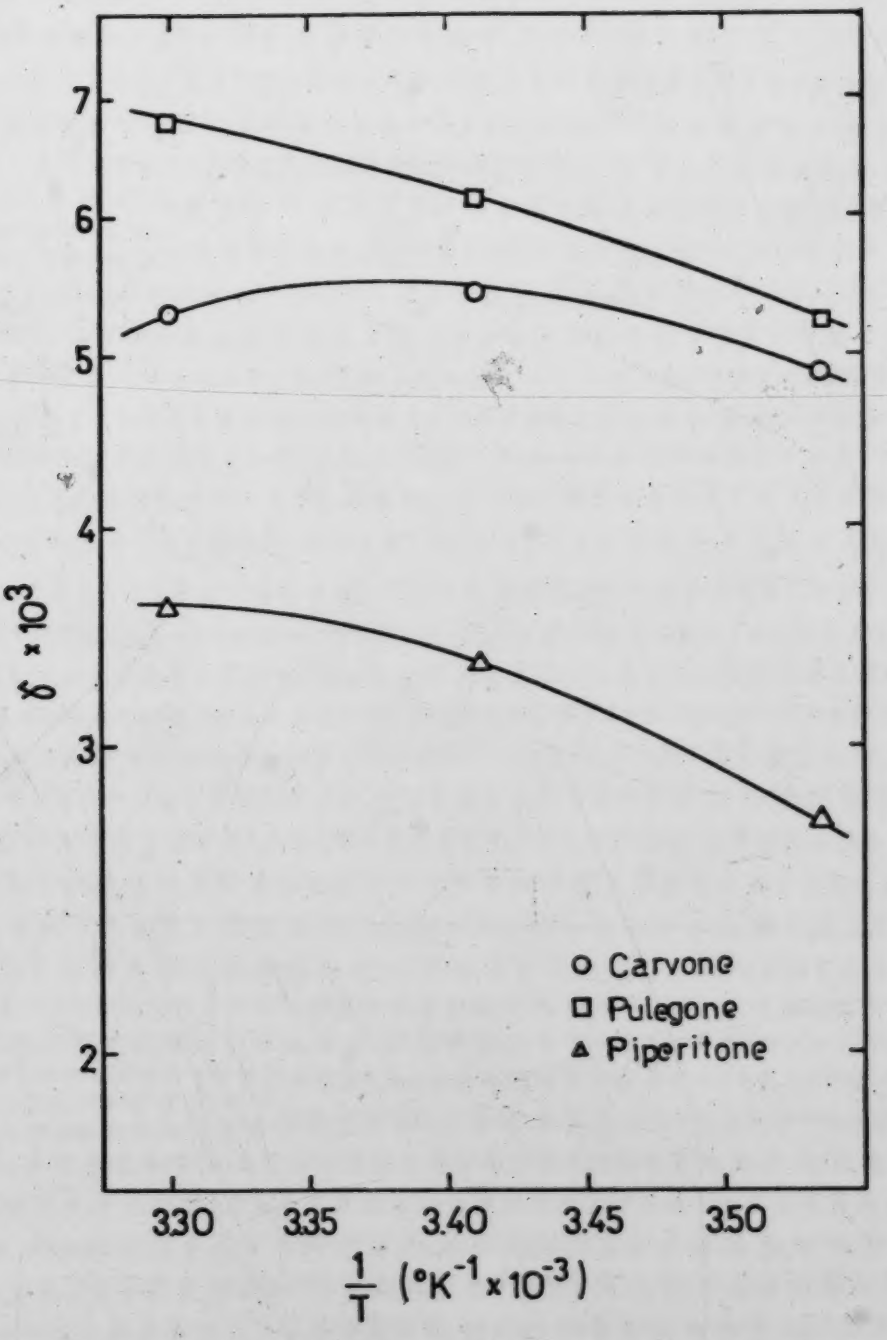


Figure 51. Curves relating γ and T in the determination of ΔHs for piperitone, pulegone and carvone in water.

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V. Appendices

APPENDIX 1 Derivation of Equation(5)

The equation required to calculate the diffusion coefficient for a two-compound system from measurements of the concentration gradient in a free diffusion experiment is given by Longsworth (1945),

$$\frac{\partial c}{\partial x} = \frac{\Delta c}{2\sqrt{\pi D t}} e^{-x^2/4Dt} \qquad (1)$$

where Δc is the concentration difference of the diffusing substance, D is the diffusion coefficient and c is the concentration at a distance x from the interface at time t. The term $\partial c/\partial x$ refers to the actual concentration gradient within the diffusion cell.

The dimensions of the cell are magnified by the lenses of the schlieren optical system. The camera lens magnifies the schlieren curve both in the x and y directions and this magnification by the camera lens is represented by the magnification factor, m_1. The cylindrical lens magnifies the schlieren curve only in the y direction and gives rise to the magnification factor, m_2. Therefore the displacement in the y direction as seen on the film is,

$$Y = La \frac{dc}{dx} \frac{dn}{dc} \frac{m_1 m_2}{\tan\theta} \qquad (2)$$

where L is the distance from the middle of the cell to the plane of the schlieren analyzer, a is the thickness of the diffusion cell, dn/dc is the refractive index increment and θ is the angle of the schlieren analyzer. The displacement in the y direction is seen to be influenced by both m_1 and m_2. However the displacement in the x direction as recorded on film is only a function of m_1,

$$X = m_1 x \qquad (3)$$

where x again refers to cell dimensions.

Enlargement of the image using the slide projector introduces an additional magnification factor, β_1, which is equal for both x and y directions. Therefore the displacements in the y and x directions as registered on the projected image are given by Equations (4) and (5) respectively.

$$y' = \beta_1 La \frac{dc}{dx} \frac{dn}{dc} \frac{m_1 m_2}{\tan\theta} \qquad (4)$$

$$x^1 = \beta_1 X = m_1 x \beta_1 \qquad (5)$$

The quantities y^1 and x^1 are values measured on the vertical gradient.

Equation (4) may be rearranged to yield Equation (6).

$$\frac{dc}{dx} = \frac{y^1 \tan\theta}{\beta_1 La \frac{dn}{dc} m_1 m_2} \qquad (6)$$

Equation (6) relates the concentration gradient in the diffusion cell to the measured quantity y^1.

Substitution of Equation (5) and (6) into Equation (1) yields,

$$y^1 = \frac{\alpha \Delta c}{2\sqrt{\pi D t}} e^{-(x^1)^2/\beta^2 4Dt} \qquad (7)$$

where

$$\alpha = \frac{\beta_1 \, La \, m_1 m_2 \, \frac{dn}{d\theta}}{\tan\theta} \qquad (8)$$

$$\beta = \beta_1 m_1 \qquad (9)$$

β is the overall magnification in the x direction and is obtained from the measurement of the reference lines in the counterbalance of the Analytical-D rotor.

Rearranging Equation (7) and taking the natural logarithms yields Equation (10).

$$\ln(y^1 t^{\frac{1}{2}}) = \ln \frac{\alpha \Delta c}{2\sqrt{\pi D}} - \frac{x^{1^2}}{\beta^2 4Dt} \quad (10)$$

Equation (10) corresponds to Equation (5) of the text. Since α, Δc, π, D and β are all constants for a particular diffusion experiment, a plot of $\ln(y^1 t^{\frac{1}{2}})$ vs. $(x^1)^2/t$ yields a straight line of slope $-1/\beta^2 4D$ and an intercept of $\ln(\alpha \Delta c/2\ \pi D)$ and thus permits a calculation of D from the slope.

APPENDIX 2 Program for Calculation of D

```
DIMENSION Y(15,8),T(15),YO(15),X(11),Z(200),XT(200)
DIMENSION TO (15)
DATA X/0.,1.,2.,3.,4.,5.,6.,7.,8.,9.,10./
READ(1,100)N
DO 1 1=1,N
READ(1,110)DC,B,C1,C2,DX
READ(1,100)N1
DO 4 M=1,N1
READ(1,120)T(M),(Y(M,J),J=1,8)
N12=N1/2
DO 6 M=1,N12
DO 5 J=1,8
Z(J)=ALOG((Y(2*M-1,J)+Y(2*M,J))/2.SORT(T(2*M-1)))
XT(J)=(X(J)*DX)**2/T(2*M-1)
CALL SLIN1(XT,Z,8,A1,B1,0)
YO(M)=EXP(-B1)*SORT(T(2*M-1)
TO(M)=SORT(T(2*M-1))
YM=1./YO(M)
YM1=Y(2*M-1,1)
TM=T(2*M-1)
WRITE(6,150)TM,YM,YM1
CALL SLIN1(TO,YO,N12,A0,B0,0)
FORMAT(2X,3(E12.5))
DT=B0/A0
WRITE(6,140)DT
FORMAT(10X,'ZERO TIME CORRECTION =',F7.2)
K=0
D0 3 J=1,N1
TC=T(J)+DT
D0 2 L=1,8
IF(Y(J,L).EQ.0.)GO TO 3
K=K+1
Z(K)=ALOG(Y(J,L)*SORT(TC))
XT(K)=(X(L)*DX)**2/TC
CONTINUE
CONTINUE
CALL SLIN1(XT,Z,K,A1,B1,0)
D=-1./(4.*B*B*A1)*1.E-6
ALPHA=2.*SORT(3.14159*D)*EXP(B1)/DC
CAV=(C1+C2)/2.
WRITE(6,130)DC,B,CAV,D,ALPHA
FORMAT(12)
FORMAT(5E12.5)
FORMAT(12E10.3)
FORMAT(2X,'DC=',F7.4,2X,'MAGNIFICATION=',F7.3,/,2X,'C=',
```

```
F7.4,
*2X,'DIFFUSION COEFFICIENT =',E12.5,2X,'ALPHA=',E12.5/)
CONTINUE
STOP
END
```

APPENDIX 3 Determination of the Zero Time Corrections

Because the starting boundary may not be perfectly sharp, use of the observed times, t^1, may lead to slightly erroneous values/D. Therefore all values of t, employed in calculating D are corrected by using the zero time correction, Δt.

$$t = t^1 + \Delta t$$

The zero time correction is calculated from a plot of $1/(hmax)^2$ vs. t^1, where hmax is the height of the schlieren peak at x=0 for the photograph taken at time t^1. Δt values correspond to the intercept on the t^1 axis. In all cases Δt has been calculated from a least squares analysis of $(1/hmax)^2$ and t^1, and the corrected t^1 values, i.e. t, have been incorporated into the linear regression from which the diffusion coefficients are calculated (Equation (5) of text).

APPENDIX 4 Equation for Calculating ΔG_h

The chemical potential of a dilute volatile component (i) in aqueous solution is given by the expression,

$$\mu_i^L = \mu_i^* + RT\ln X_i\gamma_i$$

where μ_i^L = chemical potential of the volatile solute in a dilute aqueous solution
μ_i^* = standard chemical potential of the volatile solute in an infinitely dilute reference state
R = gas constant
T = absolute temperature
X_i = mole fraction of the solute in solution
γ_i = activity coefficient of the volatile solute

The chemical potential of the volatile solute in the headspace above the solution is given by the expression,

$$\mu_i^v = \mu_i^o + RT\ln p_i$$

where μ_i^v = chemical potential of volatile solute in the headspace above the solution
μ_i^o = standard chemical potential of volatile solute in the pure gaseous reference state
p_i = vapor pressure of the volatile

At equilibrium, $\mu_i^L = \mu_i^v$, hence

$$\mu_i^* - \mu_i^o = RT\ln\frac{pi}{X_i\gamma_i}$$

Using an infinitely dilute reference state (γ_i=1) at saturation (X_i=X_s),

$$\mu_i^* - \mu_i^o = \Delta Gh = RT\ln\frac{pi}{Xs}$$

This Equation corresponds to Equation 2 in Part III of the text.

APPENDIX 5 Equation for Calculating ΔH_s

The chemical potential for a dilute volatile component (i) in aqueous solution is given by the expression,

$$\mu_i^L = \mu_i^* + RT\ln X_i\gamma_i$$

where μ_i^L = chemical potential of the volatile component in a dilute aqueous solution
μ_i^* = standard chemical potential of the pure liquid volatile component at a specified temperature and pressure
X_i = mole fraction of the volatile solute in the solution
γ_i = activity coefficient of the volatile solute in the solution

Dividing by T and differentiating with respect to T (P, X = constant)

$$\frac{\partial \frac{\mu i^L}{T}}{\partial T} = \frac{\partial \frac{\mu i^*}{T}}{\partial T} + \frac{R\partial \ln Xi}{\partial T} + \frac{R\partial \ln \gamma i}{\partial T}$$

But $$\frac{\partial \frac{\mu i^L}{T}}{\partial T} = \frac{-\bar{H}i^L}{T^2} \quad \text{and} \quad \frac{\partial \frac{\mu i^*}{T}}{\partial T} = \frac{-hi^L}{T^2}$$

Therefore $$\frac{-\bar{H}i^L}{T^2} = \frac{-hi^L}{T^2} + \frac{R\,\partial \ln \gamma i}{\partial T}$$

$$\frac{\partial \ln \gamma i}{\partial T} = \frac{hi^L - \bar{H}i^L}{RT^2}$$

This expression may be rearranged to

$$\frac{\partial \ln \gamma i}{\partial \frac{1}{T}} = \frac{\bar{H}i^L - hi^L}{R} = \frac{\Delta Hs}{R}$$

This Equation corresponds to Equation 4 in Part III of the text.